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Quality Assurance Project Plan

Salish Sea Dissolved Oxygen Modeling Approach:
Sediment-Water Interactions

Publication Information

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Quality Assurance Project Plan

Salish Sea Dissolved Oxygen Modeling Approach: Sediment-Water Interactions

July 2014

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EAP: Environmental Assessment Program

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Abstract

Low concentrations of dissolved oxygen have been measured throughout the Salish Sea. Recent modeling investigations indicate that low concentrations occur throughout much of the Salish Sea due to the Pacific Ocean and natural conditions. However, some regions of South and Central Puget Sound are also influenced by human nutrient contributions. Sediment-water interactions strongly influence oxygen levels. The previous modeling studies externally specify the sediment-water exchanges and adjustments to account for changes in external loading. That approach cannot distinguish the loading and sediment effects of individual sources.

The purpose of this model development is to add the capability to dynamically simulate the sediment-water exchanges in a process called sediment diagenesis. Material fluxes to the sediment from the water column fuel biogeochemical processes that release some of the nutrients back to the water column and consume oxygen in the process. We will set up and test the model code to ensure that sediment-water exchanges are incorporated appropriately.

We will apply the revised model to the Salish Sea and compare against monitoring data to assess the model skill. If needed, we will recalibrate the dissolved oxygen model. The revised model will be used to reevaluate scenarios to identify the relative influences of climate effects, local human nutrient sources, and the Pacific Ocean on dissolved oxygen. Results also will be used to develop new boundary conditions for the South and Central Puget Sound model.

Introduction and Background

The Department of Ecology recently completed an analysis of the relative influences of human nutrient sources and Pacific Ocean influences on dissolved oxygen concentrations in Puget Sound, the Strait of Georgia, and the Strait of Juan de Fuca. This region is collectively known as the Salish Sea. The calibrated model was applied to a series of scenarios to isolate the influence of different sources now and into the future (Roberts et al., 2014). Results indicate that human nitrogen contributions from the U.S. and Canada have the greatest impacts on dissolved oxygen in South and Central Puget Sound. Marine point sources cause greater decreases in dissolved oxygen than watershed inflows compared with natural conditions.

Separately, the Department of Ecology developed a three-dimensional circulation and water quality model of South and Central Puget Sound with an external boundary at Edmonds. The calibrated model was applied to a series of scenarios to isolate the effects of different sources, including local human nutrient sources (Ahmed et al., 2014). We used the Salish Sea model to assess the change in water quality at the Edmonds boundary that would result from eliminating human sources in the Salish Sea under natural conditions. The relationship was then used to adjust the boundary to account for different external load scenarios.

The Salish Sea model was calibrated by specifying sediment-water exchanges of nitrogen and oxygen (Khangaonkar et al., 2012 a,b). Very little is known about sediment fluxes in Puget Sound (Sheibley and Paulson, 2014). Most available information focuses on shallow regions of Puget Sound in the late summer, but those express a wide range of magnitudes. The Budd Inlet Scientific Study (Aura Nova Consultants et al., 1998) provided the most complete year-round assessment of fluxes and found that fluxes generally peak in the late summer months, but display high variability.

To assess sediment-water exchanges under different load scenarios, we calculated scalars (scaling factors) from a mass balance of external loads to the region south of Whidbey Island where the majority of the U.S. human sources originate. However, these scalars reflected total loads of nitrogen and were not specific to an individual source. We applied the sediment scalars to the entire region and were unable to develop spatially heterogeneous sediment fluxes.

Sediment diagenesis refers to the process where biogeochemical processes transform the nutrients delivered to the sediments from particles settling from the water column and release a portion of the nutrients back into the water column (Figure 1). The process also consumes oxygen. A portion of the nutrients are buried as well, where they are permanently lost from the active system.
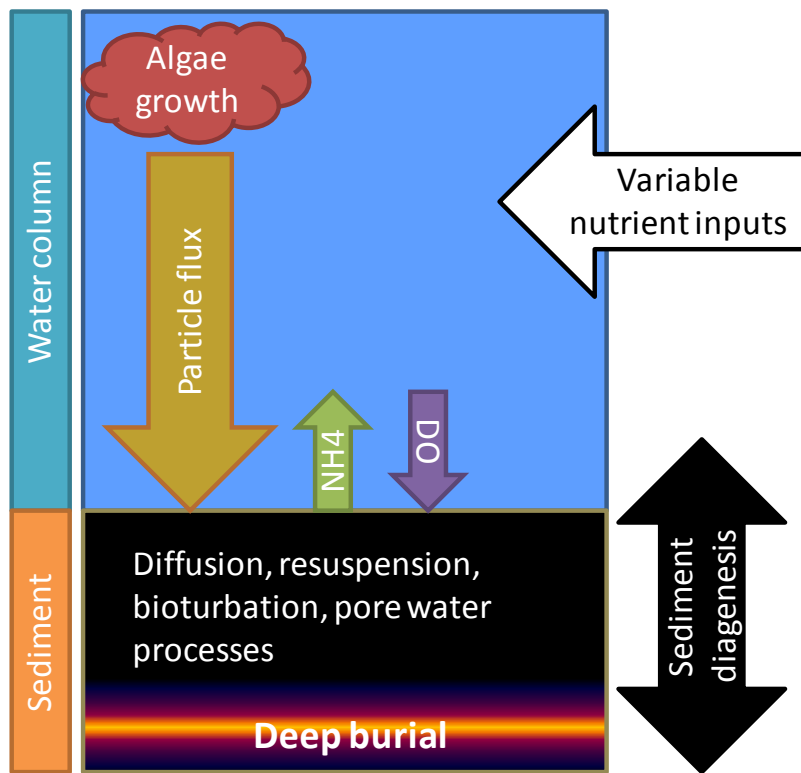
Figure 1. Sediment diagenesis schematic

The Pacific Ocean, natural sources, and human activities are sources of nutrients to the Salish Sea. Nutrients that reach the euphotic zone, where there is sufficient light, spur phytoplankton growth. These nutrients include a combination of inputs from rivers and the surface waters of incoming tides, as well as deeper sources of nutrients from deep discharges and the bottom waters of incoming tides that are mixed up into the water column. This vertical mixing is especially important across shallow sills, such as the Tacoma Narrows and Admiralty Inlet. Buoyant processes can also mix deeper nutrients into surface waters.

As the algae bloom, they transform dissolved material into particulate matter. As the algae die, they settle to the bottom. Zooplankton that feed on the algae also produce wastes that settle to the bottom as a flux of particles. These combined fluxes fuel processes within the sediments.

A variety of physical and biogeochemical processes act on the organic matter in the sediments. The organic matter decomposes in the sediment. Plants and animals physically rework the sediments. Decomposition and oxidation of organic matter transforms nutrients and release them back to the water column. Sediment oxygen levels decline from bottom water concentrations to near zero within a few centimeters of the surface, which produces strong gradients. These gradients contribute to diffusion into the sediments as oxygen is used to fuel decomposition of organic matter. This exerts a sediment oxygen demand on the water column. The decomposition of organic nitrogen generates ammonium and also creates a gradient that pushes ammonium out of the sediments and into the water column.

Sediment diagenesis refers to the decomposition of organic matter that is deposited from the water column into the sediments, the sediment processes that transform organic matter into other forms, and the fluxes between the sediments and water that result. In addition, not all of the particle flux is returned to the water column. A portion of the particles are lost from the system as deep burial.

The purpose of this model development is to add the capability to dynamically simulate sediment diagenesis. In addition to developing and implementing the code changes needed to simulate this process, this process will also extensively test the revised code to verify the correct model connections and behavior under idealized conditions. The revised model will then be applied to the calibration period. If this comparison finds major differences in model skill, then the Salish Sea dissolved oxygen model may need to be recalibrated. The final calibrated model will be applied to the Salish Sea scenarios to evaluate the relative effect of human nutrient sources and the Pacific Ocean. The Salish Sea model will also be used to refine boundary conditions for the South and Central Puget Sound dissolved oxygen model.

Study Area

The Salish Sea refers to the region covered by Puget Sound, the Strait of Georgia, and the Strait of Juan de Fuca (Figure 2). Pacific Ocean water enters the Salish Sea primarily through the Strait of Juan de Fuca, with a lesser exchange around the north end of Vancouver Island in Canada through Johnstone Strait. The marine water model domain (Figure 3) includes portions of the US and Canada.
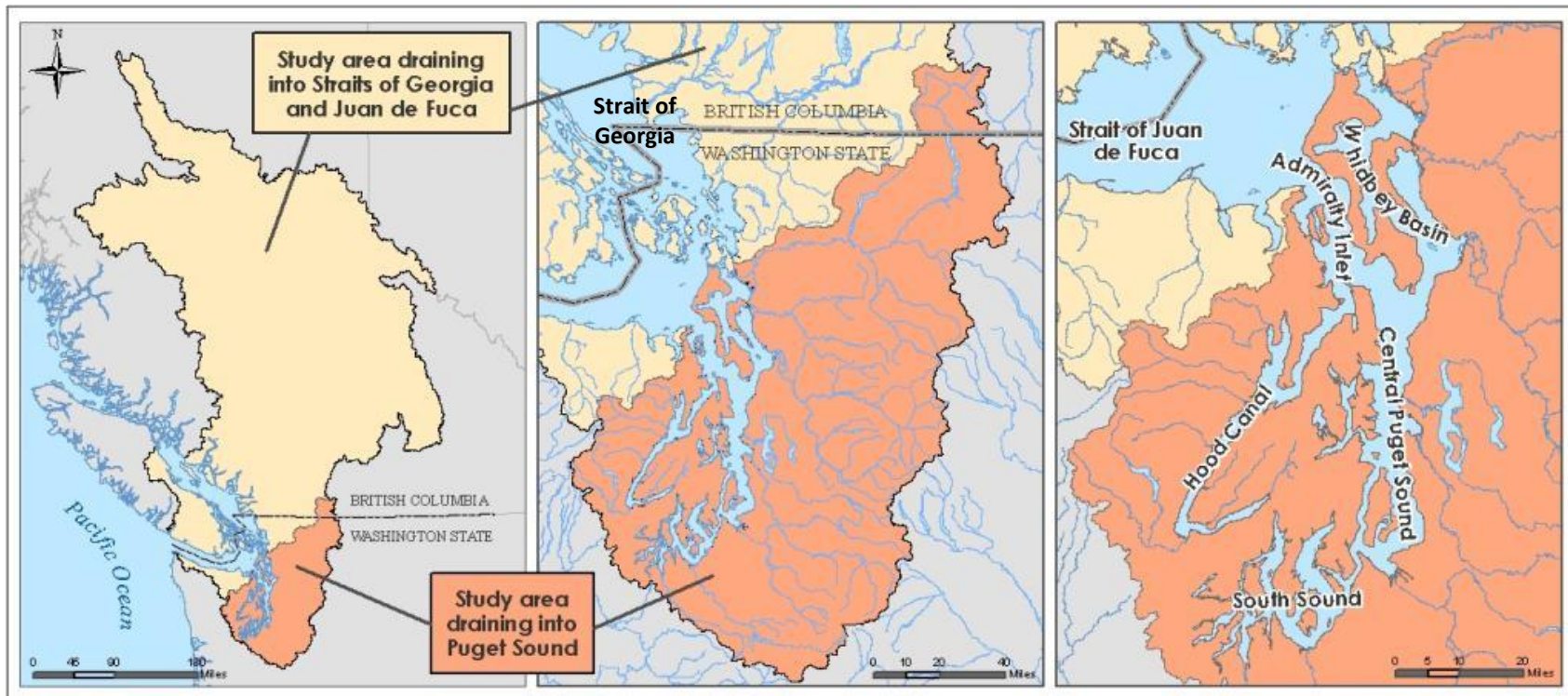
Figure 2. Puget Sound and the Straits of the Salish Sea with land areas discharging to marine waters within the model domain.
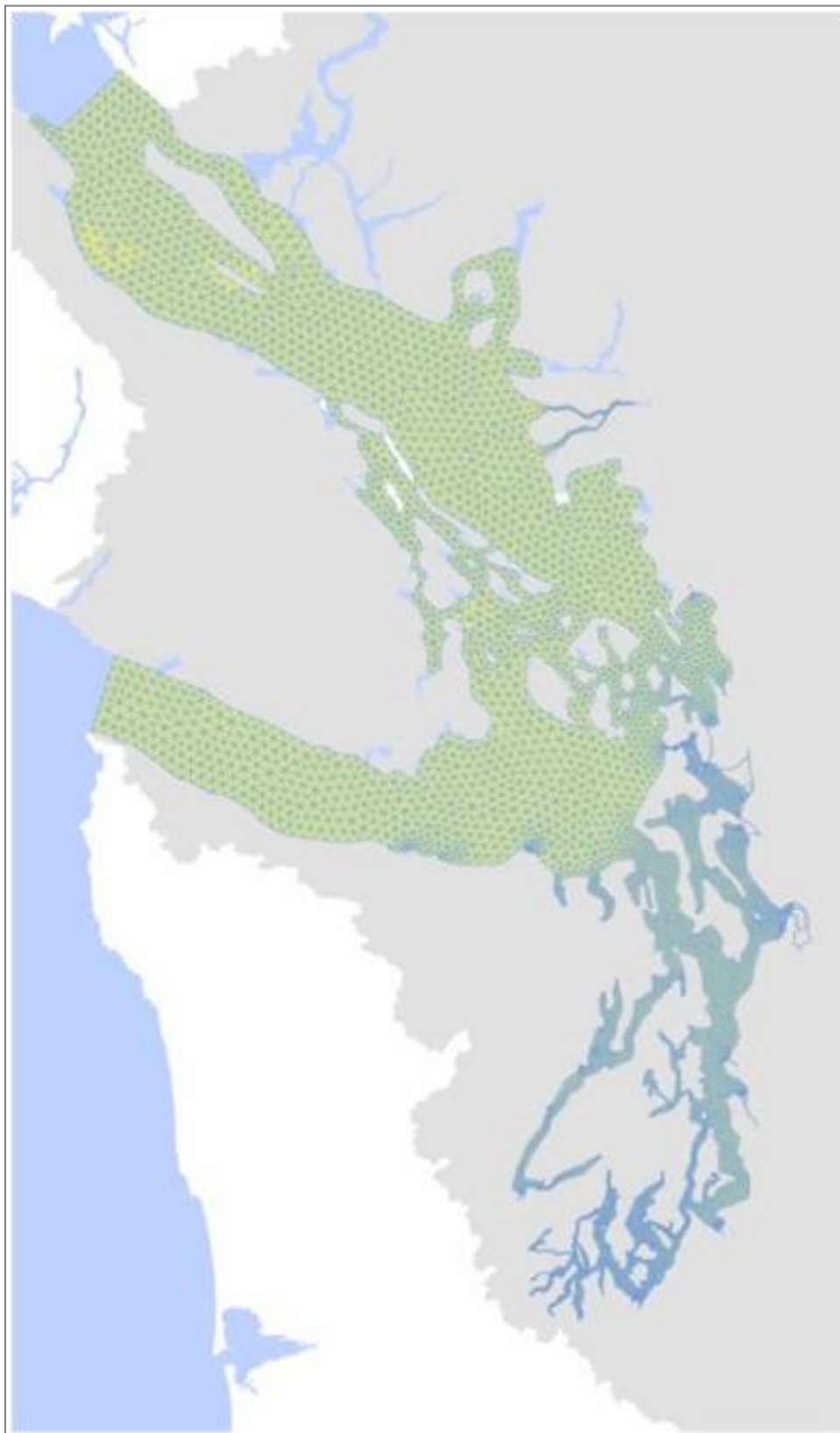
Figure 3. Salish Sea model computational grid.

Freshwater from the Salish Sea watershed enters through rivers, streams, and other inflows, where they mix with the marine waters (Mohamedali et al., 2011). The Fraser River represents the largest single source of freshwater overall and much of the 4,200 m^3/s of Canadian freshwater inflow in 2006. The largest source of freshwater to Puget Sound is the Skagit River. U.S. watershed inflows totaled 1,500 m^3/s to Puget Sound and an additional 300 m^3/s to the Straits in 2006 with some interannual variability. These freshwaters deliver nitrogen, predominantly in nitrate form, to the estuarine environment. In 2006, U.S. watersheds delivered 27,500 kg/d of dissolved inorganic nitrogen (DIN) to Puget Sound and an additional 7,300 kg/d to the Straits from the combined effect of natural and human sources. Canadian watersheds delivered 44,400 kg/d of DIN, dominated by the Fraser River with 33,500 kg/d. These include the combined effect of natural and human sources within the watersheds.

Other sources of freshwater and nitrogen include wastewater treatment plants. Marine point sources deliver much less flow than the watersheds. U.S. marine point sources produce 20 m^3/s and Canadian marine point sources about 16 m^3/s. However, nitrogen is more concentrated in treatment plant effluent and can be 10 to 30 mg/L of total nitrogen, nearly all of which is DIN. This results in loads from treated wastewater of 34,700 kg/d from U.S. treatment plants and 29,100 kg/d of DIN from Canadian treatment plants in 2006. Nearly all of the wastewater is from municipal wastewater; a small fraction is from industrial wastewater.

The largest wastewater inputs serve the largest metropolitan areas. Five treatment plants serve the greater Vancouver, BC, population of 2.2 million people, and produced 25,800 kg/d of DIN in 2006. Two outfalls serve the Seattle metropolitan area with about 1.8 million people, delivering 19,500 kg/d of DIN in 2006.

Estuarine waters exhibit highly complex circulation patterns. These reflect the intricate horizontal shape of the Salish Sea as well as the bathymetry. Shallow sills occur at the entrances to various basins, including Hood Canal, Admiralty Inlet, and the Tacoma Narrows. Shallow water depths coupled with large tidal exchanges result in strong currents and vertical mixing. Stratification affects vertical mixing throughout the Salish Sea as well.

Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area

The study area includes Water Resource Inventory Areas (WRIAs) 1 through 19 and eight-digit Hydrologic Unit Code (HUC) numbers 17110001 through 17110021.

Project Description

The Salish Sea model externally specifies the sediment fluxes of nitrogen and oxygen (Khangaonkar et al., 2012 a,b). These were adjusted to account for changes in external nutrient loading and flow while evaluating alternative natural, current, and future loads (Roberts et al., 2014). Higher loads would cause additional phytoplankton growth, higher particulate deposition to the sediments, and higher exchanges of nitrogen and oxygen. This phase of model

development will incorporate sediment processes directly so that they are calculated internally to the model and reflect changes in loading or other processes.

This project will include several tasks:

- Implement software changes to connect sediment-water interactions to model code.
- Test software changes on idealized systems with analytical solutions.
- Apply updated code to Salish Sea system and check against monitoring data.
- Recalibrate dissolved oxygen (if needed).
- Evaluate relative influences of local human nutrient sources and the Pacific Ocean by revisiting current scenarios described in Roberts et al. (2014).
- Document findings.

The follow-up application to the South and Central Puget Sound model scenarios will follow this project.

Intended Use of the Model

This Salish Sea model application has two uses. First, the Salish Sea model will be used to develop boundary conditions for the South and Central Puget Sound model that incorporate the influence of sediment diagenesis. Boundary conditions include both water column concentrations at the northern boundary near Edmonds and bottom sediment fluxes throughout South and Central Puget Sound. Salish Sea model output will be used to adjust both the water column and sediment fluxes under alternative loading scenarios. Second, the model will be used to identify the relative influences of local human nutrient sources and the Pacific Ocean on the low concentrations of dissolved oxygen measured in Puget Sound and the Salish Sea at the Salish Sea scale. If this effort finds human sources cause >0.2 mg/L impact on dissolved oxygen compared with natural conditions beyond the South and Central Puget Sound model domain, a subsequent effort would be needed to develop load reduction targets.

Organization and Schedule

Table 1 lists the individuals involved in this project. All are employees of the Washington State Department of Ecology unless otherwise noted. Table 2 presents the proposed schedule for this project.

Table 1. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Will Kendra EA Program Statewide Coord Section Phone: 360-407-6698	Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
Mindy Roberts MIS Unit Statewide Coord Section Phone: 360-407-6804	Project Manager	Writes the QAPP. Oversees model development and application. Participates in model evaluation. Writes the draft report and final report.
Greg Pelletier MIS Unit Statewide Coord Section Phone: 360-407-6485	Modeling Advisor	Assists in writing model theory portions of the QAPP. Participates in model evaluation. Develops software tests and evaluates results.
Teizeen Mohamedali MIS Unit Statewide Coord Section Phone: 360-715-5209	Modeling Assistant	Develops boundary conditions, applies the model, and post-processes the results. Participates in model evaluation. Assists in drafting the report.
Tarang Khangaonkar Pacific Northwest National Laboratory (PNNL) Phone: 206-528-3053	PNNL Project Manager	Oversees software development and testing. Participates in model evaluation. Assists in applying the model and post-processing the results.
Wen Long Pacific Northwest National Laboratory Phone: 360-683-4151	PNNL Model Developer	Revises model software code and conducts tests specified by Ecology. Leads model evaluation. Assists in applying the model and post-processing the results.
Karol Erickson MIS Unit Statewide Coord Section Phone: 360-407-6694	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra Statewide Coord Section Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Robert F. Cusimano Western Ops Section Phone: 360-407-6596	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Andrew Kolosseus Phone: 360-407-7543	WQP Liaison	Reviews the draft QAPP, coordinates with WQP, and manages the advisory committee.
Tom Gries Phone: 360-407-6327	NEP Quality Assurance Manager	Reviews the draft QAPP and approves the final QAPP.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Approves the QAPP.

EAP: Environmental Assessment Program
MIS: Modeling and Information Support
QAPP: Quality Assurance Project Plan
NEP: National Estuary Program

Table 2. Proposed schedule for completing final report.

Field and laboratory work	Due date	Lead staff
Field work completed	Not applicable	Not applicable
Laboratory analyses completed	Not applicable	
Environmental Information System (EIM) database		
EIM user study ID	Not applicable	
Product	Due date	Lead staff
EIM data loaded	Not applicable	Not applicable
EIM QA	Not applicable	Not applicable
EIM complete	Not applicable	Not applicable
Final report		
Author lead / Support staff	Mindy Roberts / Greg Pelletier/Teizeen Mohamedali	
Schedule		
Draft due to supervisor	August 2015	
Draft due to client/peer reviewer	August 2015	
Draft due to external reviewer(s)	September 2015	
Final (all reviews done) due to publications coordinator (Joan)	October 2015	
Final report due on web	December 2015	

Project Quality Objectives and Performance Criteria

The overall modeling goal is to improve the performance of the Salish Sea dissolved oxygen model by incorporating sediment processes to better identify and quantify factors and processes that influence dissolved oxygen. Specific objectives include the ability to assess oxygen levels under natural conditions including the influences of sediments, distinguish relative impacts of current sources, and project future oxygen conditions that reflect sediment processes.

Performance criteria are based on both quantitative and qualitative measures. Quantitative measures will rely on root-mean-squared error (RMSE) and bias assessed throughout the model domain and throughout the period of simulation. Qualitative measures include the ability to reproduce seasonal patterns in dissolved oxygen, chlorophyll a as a proxy for phytoplankton, and nutrients.

We will rely on marine data collected using appropriate quality controls to evaluate RMSE and bias. These include Ecology's ambient monitoring program (www.ecy.wa.gov/apps/eap/marinewq/mwdataset.asp) and the focused South Puget Sound Dissolved Oxygen Study (Roberts et al., 2008). In addition, we will compare estimated fluxes with those compiled by Sheibley and Paulson (2014), which includes measured fluxes in South Puget Sound. We will identify available particle flux measurements as well, such as Norton (2009) from South Puget Sound inlets.

Sampling Process Design (Experimental Design)

Not applicable; no sampling is planned. See Model Theory, Model Development and Testing, and Model Calibration and Validation for model-related information.

Model Selection

Sackmann et al. (2009) describes the initial model selection, set up, and application of the Salish Sea circulation and dissolved oxygen model. We considered several needs in the initial model selection, including the ability to simulate:

- Complex horizontal shapes, including branching basins and inlets
- Highly variable bathymetry, with deep basins >200 meters, shallow inlets <20 meters, and shallow sills that divide the region into basins
- Large tidal amplitudes that produce very high velocities in constricted regions
- Regions that are dry at low tide but that contribute to biogeochemical processes
- Time-varying river inputs and human sources
- Physical, chemical, and biological processes that affect dissolved oxygen

We selected the Finite-Volume Coastal Ocean Model (FVCOM; Chen et al., 2003) to simulate three-dimensional circulation in the Salish Sea using an unstructured grid. FVCOM can simulate wetting and drying and uses a sigma grid system where the vertical layer thickness changes to simulate sea surface height. PNNL developed the linked FVCOM-ICM (Integrated Compartment Model) based on the kinetic equations of CE-QUAL-ICM (Cerco and Cole, 1995). Yang et al. (2010) and Khangaonkar et al. (2011) describe the circulation calibration and Khangaonkar et al. (2012 a,b) describes the water quality model calibration.

Roberts et al. (2014) summarizes the results of scenarios evaluated with the calibrated model and recommended additional sediment model development to support this Salish Sea modeling project as well as the South and Central Puget Sound Dissolved Oxygen Study (Ahmed et al., 2014). We will continue to develop the Salish Sea model by adding the sediment diagenesis capability.

Several modeling efforts have included sediment diagenesis in freshwater or marine environments. However, none will function with the existing Salish Sea model without model code changes. Frameworks considered for the sediment diagenesis component include DiToro et al. (1990); Martin and Wool (2013); and Morse and Eldridge (2007).

Sediment flux models range from simple empirical relationships (Fennel et al, 2006) to complex process simulations with time-varying state variables (Boudreau, 1997). Simple representations include assigning constant fluxes of sediment oxygen demand (SOD) or nutrients (Scully, 2010)

or using simple relationships with overlying water concentrations (Imteaz and Asaeda, 2000; Fennel et al., 2006; Hetland and DiMarco, 2008). More complex models may simulate one or two layers, each representing a particular chemical environment (DiToro, 2001; Emerson et al 1984; Gypens et al, 2008; Slomp et al 1998; Vanderborght et al., 1977). Sediment flux models may also be resolved into numerous layers (Morse and Eldridge, 2006; Boudreau, 1997; Dhakar and Burdrige, 1996; Cai et al., 2010). Multi-layer models have been found to fit observations better than two-layer models with some data sets (Wilson et al., 2013). However, depth resolution entails higher computational demand (Gypens et al., 2008) than two-layer models. Therefore two-layer models are often used as a compromise between computational efficiency and depth-resolution, while providing acceptable accuracy (Testa et al., 2013; Brady et al., 2013).

Water Analysis Simulation Program (WASP) uses the two-layer methods of DiToro et al. (2001). WASP is one of the most widely used water quality models in the United States and throughout the world. Because of the model's capabilities of handling multiple pollutant types it has been widely applied in the development of Total Maximum Daily Loads (TMDL). WASP incorporates a sediment diagenesis module (Martin and Wool, 2013) that is based on DiToro's (2001) framework, and is nearly identical to the module that is also used in CE-QUAL-ICM.

Di Toro et al. (1990) developed a model of sediment oxygen demand (SOD) that has gained wide adoption in estuarine modeling frameworks such as those of Cerco and Cole (1995), Chapra (1997), and Martin and Wool (2013). Di Toro's approach (Di Toro, 2001) calculates sediment oxygen demand and the release of nitrogen and phosphorus as functions of the downward flux of carbon, nitrogen, and phosphorus from the water column. This approach, well founded in diagenetic theory and supported by field and laboratory measurements, was an important advancement in the field of sediment-water interactions.

We selected the WASP sediment diagenesis routines because they have been found to provide an acceptable level of complexity with sufficient accuracy, are well documented, applied to a wide range of freshwater and marine water systems, and broadly vetted by the modeling community.

Model Theory

Sediment Flux Model

The sediment flux model (SFM) we propose to use is based on the well-documented WASP modeling framework developed by USEPA (Martin and Wool, 2013). The structure for the SFM integrates four processes illustrated in Figure 3:

1. Deposition of particulate organic carbon (C) and nitrogen (N), collectively referred to as particulate organic matter (POM), from the water column into the sediment. This includes all forms of particulate organic matter from phytoplankton and detritus.

2. Decomposition of POM in the sediment, producing dissolved forms of C and N in the sediment pore water. The process of decomposition of POM is called diagenesis.

3. The solutes formed by diagenesis react and are transported between a thin aerobic layer at the surface of the sediment and a thicker anaerobic layer of sediment below the aerobic layer, or are released as gases (methane and nitrogen gas).

4. Solute forms of C and N are returned to the overlying water and dissolved oxygen (DO) from the overlying water is transferred from the overlying water into the sediment to supply the oxidation of solutes (dissolved organic C and ammonium) in the aerobic sediment layer.

The SFM numerically integrates the mass balance equations for chemical constituents in two layers of sediment (Figure 4):

- Layer 1: A relatively thin aerobic layer at the sediment water interface with variable thickness

- Layer 2: A thicker anaerobic layer with thickness equal to the total sediment depth of 10 cm[1] (DiToro, 2001) minus the depth of the aerobic layer.
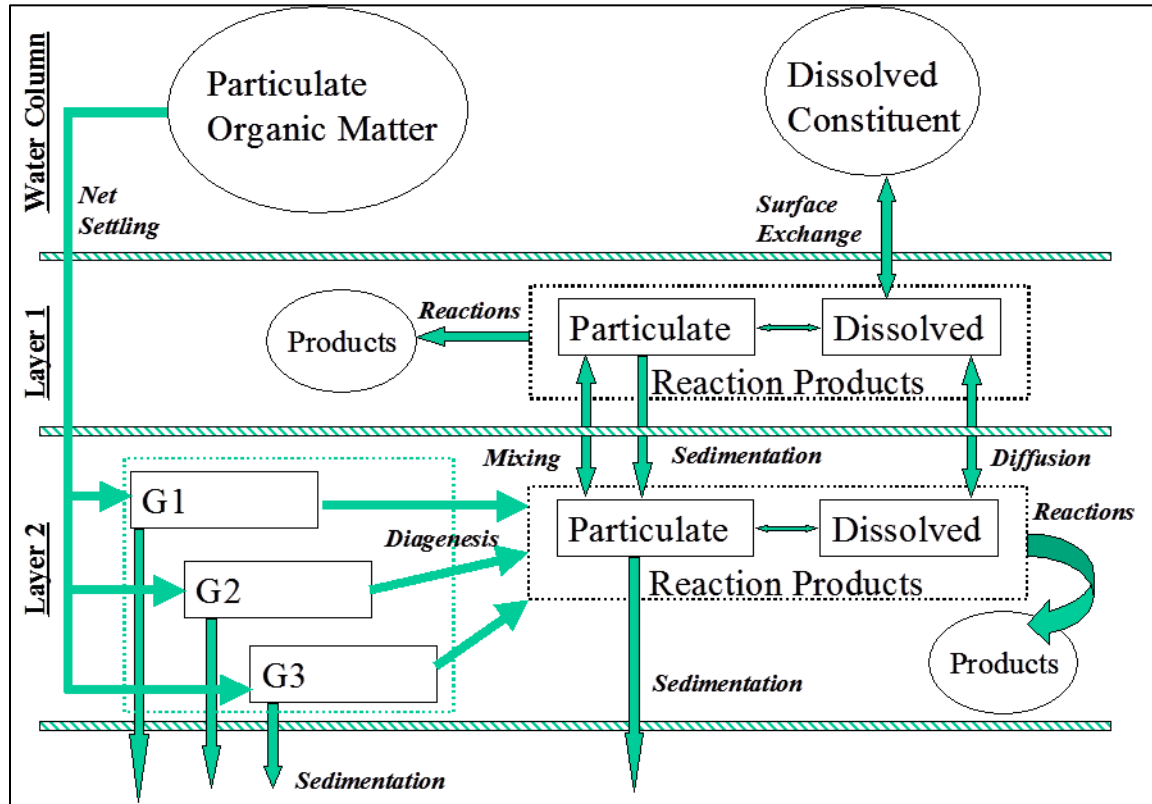
Figure 4. Basic structure of the sediment flux model (Martin and Wool, 2013).

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[1] Boudreau (1994) found that worldwide mean from 200 cores in estuarine and marine sediment had bioturbation zone thickness of 9.8 +/- 4.5 cm. Carpenter et al. (1985) found that the thickness of the bioturbated upper layers in sediment cores from the main basin ranged from about 4 to 18 cm. Lavelle et al. (1986) reported that the bioturbated upper layers in Puget Sound ranged from about 5 to 40 cm. The median thickness if the upper bioturbated layer of sediment from 63 cores in these two studies was 12 cm with inter-quartile range of 10 to 30 cm. DiToro (2001) identifies the bioturbation depth as the depth of the active layer because that is the depth to which sediment solids are mixed leading to greater homogeneity in this region.

POM initially decomposes rapidly in the sediments, but then slows down. In order to capture this process, the settled POM is fractioned to one of three "G classes" based on overall reactivity (Figure 1 in Di Toro 2001). The three G classes represent a relatively rapidly decomposing labile class (G1), a more refractory form (G2) and a relatively inert form (G3). The decomposition of the three G classes of POM occurs in layer 2. These and other parameter values will be selected based on published values in DiToro's (2001) Table 15.5. More recent published values by Testa et al. (2013) and others may be used for guidance to constrain parameter values.

The mass balance equations are solved for the concentration at the present time step during the numerical integration using information from the previous time step and the new deposition of POM during the present time step. Once the concentrations at the present time step are computed, the diagenesis source terms for reactions and transfers are computed. Diagenesis source terms are computed for C and N from the sum of the product of the chemical-specific reaction velocities and computed concentrations in each of the three G classes.

Once the sediment particulate organic matter (C and N) concentrations and source terms are computed for the present time step, the reactions and transfers are computed. Concentrations of ammonia, nitrates, methane, sulfates, and sulfides in sediment layers are computed, and then used to compute fluxes to the overlying water column, including sediment oxygen demand from the water by the sediments.

The total chemical (C, N) concentrations are computed from mass balance relationships for each of the two sediment layers. Since the surface layer is thin compared to the active anaerobic layer, fluxes from the surface layer to the water column are faster than fluxes from layer 2 to the surface layer. Therefore, layer 1 is at steady-state in comparison to the slower processes occurring in layer 2. The thickness of the layers is assumed to be constant. The equations are conveniently solved for the new concentrations using a matrix solution.

Once the concentrations have been updated, the flux of the material to the overlying water column is computed. Given the chemical concentrations in layer 1, the SOD and release rates are then computed. However, each of these constituents affects SOD, which in turn affects the surface transfer rate. Therefore, an iterative solution is required. The procedure employed in the sediment diagenesis model is as follows:

1. Start with an initial estimate of the SOD.
2. Solve layer 1 and 2 equations (for ammonia, nitrate, sulfate, sulfide, and methane).
3. Refine the estimate of SOD. A root finding method is used to make the new estimate.
4. Go to step (2) if no convergence.

There are two choices for estimating the initial conditions of concentrations of constituents in the sediment layers:

- Option 1: The initial conditions may be specified by the user as an input to the SFM. Specified initial conditions would ideally be derived from field measurements of POM subdivided into G-classes. In practice, the lack of field data and/or accepted analytical procedures from fractionating G-classes makes this difficult.

- Option 2: Alternatively, the SFM can compute the initial conditions assuming the sediment is at steady-state with the initial depositional fluxes of POM to the sediment layer (based on initial settling fluxes).

A detailed description of the model theory and all of the equations in the SFM are provided in Appendix A excerpted from Martin and Wool (2013).

Input arguments to the SFM subroutine for each time step during the numerical integration in FVCOM-ICM include the following:

- steadystate = boolean (true = steady state model per DiToro (2001) part II-III; false = time variable model per DiToro part IV). Steady state will be assumed before the first time step to estimate initial conditions. Time variable solution will be used for each time step following the initial condition.

- tc = calculation time step (days) used for time variable model (if steadystate = false)

- Jcin = flux to sediments from settling organic carbon from phytoplankton and detritus in oxygen equivalent units (g-O_2/m^2/d) (NOTE: g-O_2/m^2/d = g-C/m^2/d * 2.67 g-O_2/g-C)

- Jnin = nitrogen flux in settling phytoplankton and detritus (g-N/m^2/d)

- O20 = dissolved oxygen in water overlying the sediment (mg-O_2/L)

- depth = total water depth overlying the sediment (m) (used to calculate methane saturation concentration at in situ pressure)

- Tw = temperature in water overlying the sediment (deg C)

- NH30 = ammonia N in water overlying the sediment (mg-N/L)

- NO30 = nitrate N in water overlying the sediment (mg-N/L)

- CH40 = fast reacting dissolved organic carbon and CBODu in the water overlying the sediment in oxygen equivalent units (mg-O_2/L) (NOTE: mg-O_2/L = mg-C/L * 2.67 mg-O_2/mg-C)

- SALw = salinity in the water overlying the sediment (ppt)

Outputs from the SFM during each time step are the following:

- Output sediment concentrations – For time-variable model: these are inputs at the beginning of time step and outputs at the end of the time step. Values are initialized on the first calculation step using the steady state model)
    - NH3Tp2(1) and NH3Tp2(2) = total ammonia N in the sediment layers 1 and 2 (mg-N/L)

- o NH3p2(1) and NH3p2(2) = dissolved ammonia N in the sediment layers 1 and 2 (mg-N/L)

- o NO3p2(1) and NO3p2(2) = dissolved nitrate N in the sediment layers 1 and 2 (mg-N/L)

- o CH4p2(1) = dissolved methane in the aerobic sediment layer 1 (O_2 equivalent units mg-O_2/L)

- o HSTp2(1) and HSTp2(2) = total sulfide in sediment layers 1 and 2 (O_2 equivalent units mg-O_2/L)

- o HSp2(1) and HSp2(2) = dissolved sulfide in sediment layers 1 and 2 (O_2 equivalent units mg-O_2/L)

- o BEN_STRp2 = accumulated benthic stress2 of organisms living in the aerobic layer (days)

- o NH3(1) = dissolved ammonia N in the aerobic sediment layer 1 (mg-N/L)

- o NH3(2) = dissolved ammonia N in the anaerobic sediment layer 2 (mg-N/L)

- o NO3(1) = dissolved nitrate N in the aerobic sediment layer 1 (mg-N/L)

- o NO3(2) = dissolved nitrate N in the anaerobic sediment layer 2 (mg-N/L)

- o HST(1) * fp1 = particulate sulfide in the aerobic sediment layer 1 (oxygen equivalent units of mg-O_2/L) (NOTE: predicted particulate sulfide may be useful for comparison with measurements of acid volatile sulfide which is the acid extractable component of inorganic sulfide in the sediment)

- o HS(2) * fp2 = particulate sulfide in the anaerobic sediment layer 2 (oxygen equivalent units of mg-O_2/L)

- o POC2(1), POC2(2), and POC2(3) = particulate organic C in G class 1, 2, and 3 in the anaerobic sediment layer 2 (g-O_2/m^3) (Note that units are converted to g-C/m^3 in the 'input-output' sheet)

- o PON2(1), PON2(2), and PON2(3) = particulate organic N in G class 1, 2, and 3 in the anaerobic sediment layer 2 (g-N/m^3)

- o H1 = thickness of the aerobic sediment layer (m) (typically 0.01 m to 0.1 m)

- o BEN_STR = accumulated benthic stress on organisms living in the aerobic sediment layer due to low dissolved O_2 (days)

- Output sediment/water fluxes and layer 1 thickness – Steady-state and time-variable models

  - o H1 = thickness of the aerobic sediment layer (m)

  - o SOD = sediment oxygen demand flux of dissolved oxygen between the water and sediment (g-O_2/m^2/d) (positive is loss of O_2 from water column)

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[2] The decay rate constant for stress will be set to 0.03 /d, based on DiToro (2001).

- o Jnh4 = flux of ammonia N between the water and sediment (g-N/m^2/d) (positive is source of NH4-N to water column)

- o Jno3 = flux of nitrate N between the water and sediment (g-N/m^2/d) (positive is source of NO$_3$-N to water column)

- o Jch4 = flux of dissolved methane, fast reacting C, and CBODu between water and sediment in O2 equivalent units (g-O$_2$/m^2/d) (positive is source of CBOD to water column) (NOTE: g-O$_2$/m^2/d = g-C/m^2/d * 2.67 g-O$_2$/g-C) (methane is not produced in salt water)

- o Jch4g = flux of methane gas bubbles between the water and sediment in O2 equivalent units (g-O$_2$/m^2/d) (positive is source of CH4 bubbles to water column) (NOTE: g-O$_2$/m^2/d = g-C/m^2/d * 2.67 g-O$_2$/gC) (methane is not produced in salt water)

- o Jhs = flux of dissolved hydrogen sulfide (COD) between water and sediment in O$_2$ equivalent units (g-O$_2$/m^2/d) (positive is source of COD to water column) (hydrogen sulfide is not produced in freshwater)

Derivatives for the following existing state variables in the FVCOM-ICM model will be modified to include the source/sink terms for exchanges between the bottom layer of the water column and the sediment:

- Phytoplankton groups (sinking loss from water column and source of Jcin, Jnin, Jpin to sediment)

- Particulate organic C (sinking loss from water column and source of Jcin to sediment)

- Particulate organic N (sinking loss from water column and source of Jnin to sediment)

- Dissolved oxygen (loss from water column for SOD)

- Ammonium (gain to water column from sediment flux)

- Nitrate + nitrite (loss/gain from water column from sediment flux)

- Fast reacting DOC/CBOD (gain/loss from water column from sediment flux)

Links with FVCOM-ICM

Khangaonkar et al. (2012 a,b) describes the development, testing, and calibration of the water quality model. In summary, FVCOM is used to develop temperature, salinity, free surface heights and elevations, velocity components, and boundary fluxes. These outputs are then used to drive the ICM kinetic equations. ICM uses 19 state variables, including two species of algae, dissolved and particulate carbon, and nutrients to simulate the carbon cycle accounting for algal production and decay and the impact on dissolved oxygen. Phytoplankton primary productivity, inorganic and organic carbon fluxes, and nitrogen sources and sinks are computed and were compared with measured data during model calibration (Khangaonkar et al., 2012 a,b).

We will modify the following subroutines and processes to couple the bottom water layer with the surface sediment layer.

- SED_READ - Subroutine to read control information for SFM

- SED_INIT - Subroutine to initiate SFM variables and parameters

- SED_ALLOC - Subroutine to allocate arrays related to SFM

- SED_DEALLOC - Subroutine to de-allocate arrays related to SFM

- SED_CALC - Subroutine to carry out SFM calculations by solving time dependent two layer sediment concentration equations for each cell. A new subroutine will be created to handle output of sediment fluxes to output files.

- SEDTSFNL - Subroutine to solve 2x2 set time varying equations for the two sediment layers

- SEDSSFNL - Subroutine to solve 2x2 set steady state equations for the two sediment layers (mainly for methane generation in the system, where a 3-layer redox process can be reduced to 2-layer under assumption of steady state)

- MODULE FILE_INFO - Module that defines water column constituents and SFM variables. The SFM arrays will be moved to SFM module and subroutine SED_INIT.

- INIT_FILE_INFO - Subroutine within Module FILE_INFO which defines water column and SFM constituents as well as file units for input and output. We expect to move file units and variables related to SFM to SED_INIT

- PARWQM - Main program of FVCOM-ICM water quality model which will issue the call to SFM module when it is activated, and also move de-allocation of sediment variables into SED_DEALLOC

- ALLOC_WQM - Subroutine used for allocating both water column water quality variables and variables related to SFM. We will move all SFM variables to SED_ALLOC.

- INPUTS-- Subroutine for reading model input files. This file will be modified to call SED_READ for reading SFM related input files.

- NITROG - Subroutine for water column nitrogen calculation, where Nitrate (NO3), Ammonia (NH4) source terms will include contributions from sediment flux of nitrate, ammonia respectively from the SFM

- OXYGEN-- Subroutine for water column oxygen calculation, where oxygen sink terms will include contribution from SFM

The following implementation/modification steps are expected:

Modularization of current code - Sediment diagenesis fluxes are connected with overlying water settling POM. A clean separation of these modules is important for stepwise testing purposes and better code management.

Input and output control - The CE-QUAL-ICM style of inputs and outputs will be retained for the most part. We will incorporate a new option to read the SFM model control variables using a simplified FORTRAN name list method. The inputs include the following

- Geometry, time step

- Reaction rates and temperature control

- Mixing rates, diffusion rates, settling rates

- Fractions of G1,G2,G3, partitioning coefficients

- Flags for various scenarios (steady state vs time dependent)

- Initial conditions for time-dependent simulation

- Output frequency and variable selection (station time series, history)

- Diagnosis outputs (mass balance, individual fluxes)

Coupling with other components of the model - The fluxes are connected to the water column. In this step, we will ensure that data transfer between these different modules are clearly defined and well organized with switches to turn on or off each connection. The focus will be on coupling SFM with water column eutrophication model in this project. The code will be designed to ensure SAV, benthic algae, suspension feeder and deposition feeder modules may be added in the future.

Parallelization - The FVCOM-ICM code was improved for parallelized operation by PNNL. Parallelization is needed for master processor to distribute and collect information on model inputs and outputs to allow faster runs through the use of multiple processors. Once SFM code is incorporated into FVCOM-ICM, the code with SFM will have to be parallelized.

Processes and parameters considered but not included

We also considered several processes and parameters but will not implement them at this time. These include:

- Submerged aquatic vegetation (SAV) – While the ICM code has considered these, we do not have spatial information on the biomass of submerged aquatic vegetation around the Salish Sea. We also lack rate process information governing interactions between submerged aquatic vegetation and water quality. We anticipate that while this could be locally important in regions such as Padilla Bay, submerged aquatic vegetation does not significantly affect sediment diagenesis or dissolved oxygen throughout the system.

- Shellfish – While the ICM code has considered shellfish, we lack fundamental information on shellfish interactions with water quality such as standing stock and rate processes governing native species (Konrad, 2014). More information is available on the Pacific oyster as a commercially valuable species, but these may not be applicable to native shellfish populations. We anticipate shellfish may be locally important in regions with extensive shellfish biomass.

- Phosphorus – ICM includes the capability of simulating soluble reactive phosphorus but does not currently include organic phosphorus. We do not recommend pursuing calibration of phosphorus given that significant resources would be needed to calibrate this state variable and we do not anticipate that phosphorus significantly limits primary productivity.

- Silica – ICM includes the capability of simulating silica but it has not been implemented or calibrated. We do not recommend pursuing calibration of silica given that significant resources would be needed to calibrate this state variable and we do not anticipate that silica significantly limits primary productivity. It may be locally important but is not likely a major influence throughout the system.

Model Development and Testing

Sackmann et al. (2009) described the information sources available for both the circulation and water quality model components, including ocean boundary conditions, meteorology, river inputs, marine discharges from wastewater treatment plants, and marine profiles and time series for model skill assessment. Khangaonkar et al. (2012 a,b) and Roberts et al. (2014) describe the final information used to calibrate the linked models and to apply the tools to several current and future water quality scenarios. Roberts et al. (2014) describes the method used to adjust sediment fluxes to account for changes in external loading in lieu of computed fluxes through sediment diagenesis in the SFM. The SFM does not require additional input data.

The SFM developed for the USEPA WASP model has previously undergone rigorous review and testing (Martin 2002). Professor James Martin at Mississippi State University has developed a stand-alone testing tool called SED_JLM.FOR that provides identical results compared with the WASP SFM. Ecology, in collaboration with Dr. Martin, has also developed an Excel VBA version of the SFM model called 'SedFlux.xlsm' that predicts nearly identical results (same within +/- 0.001%) compared with the SED_JLM.FOR (Ecology, 2013). Appendix B presents a comparison of results of Ecology's SedFlux.xlsm with Martin's SED_JLM.FOR testing tool.

Implementation and testing of the SFM into the FVCOM-ICM model of the Salish Sea will be conducted in the following steps:

1. The SFM subroutine will be written in Fortran based on the equivalent to the WASP SFM code (e.g. Sedflux.xlsm or SED_JLM)

2. The results of the SFM subroutine will be compared with SedFlux.xlsm for hypothetical conditions for a single model cell under the following scenarios:

   a. Steady-state solution of constant deposition of POM and constant overlying water quality

   b. Time-variable solution using assumed initial conditions for G classes of POM and assumed constant deposition of POM and constant overlying water quality

c. Time-variable solution using assumed initial conditions for G classes of POM and assumed time-variable deposition of POM and time-variable overlying water quality

   d. Time-variable solution using initial conditions computed assuming steady state with assumed constant deposition of POM and constant overlying water quality

   e. Time-variable solution using initial conditions computed assuming steady state with assumed time-variable deposition of POM and time-variable overlying water quality

3. The SFM subroutine will be linked with the FVCOM-ICM model of the Salish Sea. The results of the linked model for a one year simulation of existing conditions during 2006 will be compared with SedFlux.xlsm at one or more locations in the model domain.

The testing results will be summarized in an interim memo from PNNL to Ecology. This memo will be included as an appendix in the final project report. We will not proceed with applying the revised code to time-variable Salish Sea conditions until tests are completed. Results of the SFM subroutine and linked FVCOM-ICM-SFM model will be deemed adequate if the comparison with Ecology's SedFlux.xlsm model shows negligible relative differences within +/- 0.1%.

Computational Requirements

The existing model runs on a server hosted at Pacific Northwest National Laboratory. This server was purchased in 2008 and has reached the end of its working life. This section describes several options for meeting the computational needs of the next phase of model development as well as the recommended approach.

The project duration is two years. The initial SFM coding and testing phase will not require extensive computational support. However, application to the Salish Sea conditions, and potentially recalibration, will require advanced computational support during an intense phase of model development. These needs will decrease as the project progresses into scenario evaluation and documentation.

Existing Server Description and Status

The server is a Silicon Mechanics 11 twin server cluster (Rackform nServe). Each node has 8 cores, each with 22 child nodes and 1 head node for a total of 184 cores. The head node provides 32 GB of RAM and each compute child node is 16 GB. The physical dimensions are 47" high, 42" deep, and 24" wide. The power cable is 2x 12 amp, 125V. Child nodes are configured for 610 W, 626 VA, 2081 BTU/h, 5.7 Amps (110V), 3.0 amps (108V). Head nodes are configured for 401 W, 411 VA, 1369 BTU/h, 3.7 amps (110 V), and 2.0 amps (208V).

The storage space needed for a single run is 1.1 TB (33 GB for the circulation model solution, 1 TB for the circulation model NetCDF, and 36 GB for the water quality run). To execute and run the model requires 5.6 TB for export and 11.7 TB for archiving key files.

The server operating system is Linux (CentQS release 5.2). FV-COM and the adapted ICM code are not compatible with a Windows operating system. Current IP address (Eth0): 130.20.35.32. Network speeds are as follows:

- Eth0 Speed: 1.0 Mbps

- Eth1 Speed: 1.0 Mbps

- Infiniband Speed: 5.0 Gbps

Figures 5 and 6 summarize the processes for running both FVCOM and ICM. The figures also include output post-processing to develop interim graphics files for modeling team use as well as report graphics. Ecology staff access the server through a Virtual Private Network (VPN) account. PNNL requires Cyber Security Awareness Training, after which users receive a unique net ID and password along with a fob. Currently, the ICM NetCDF files are transferred to Ecology for post-processing using a series of Matlab scripts.
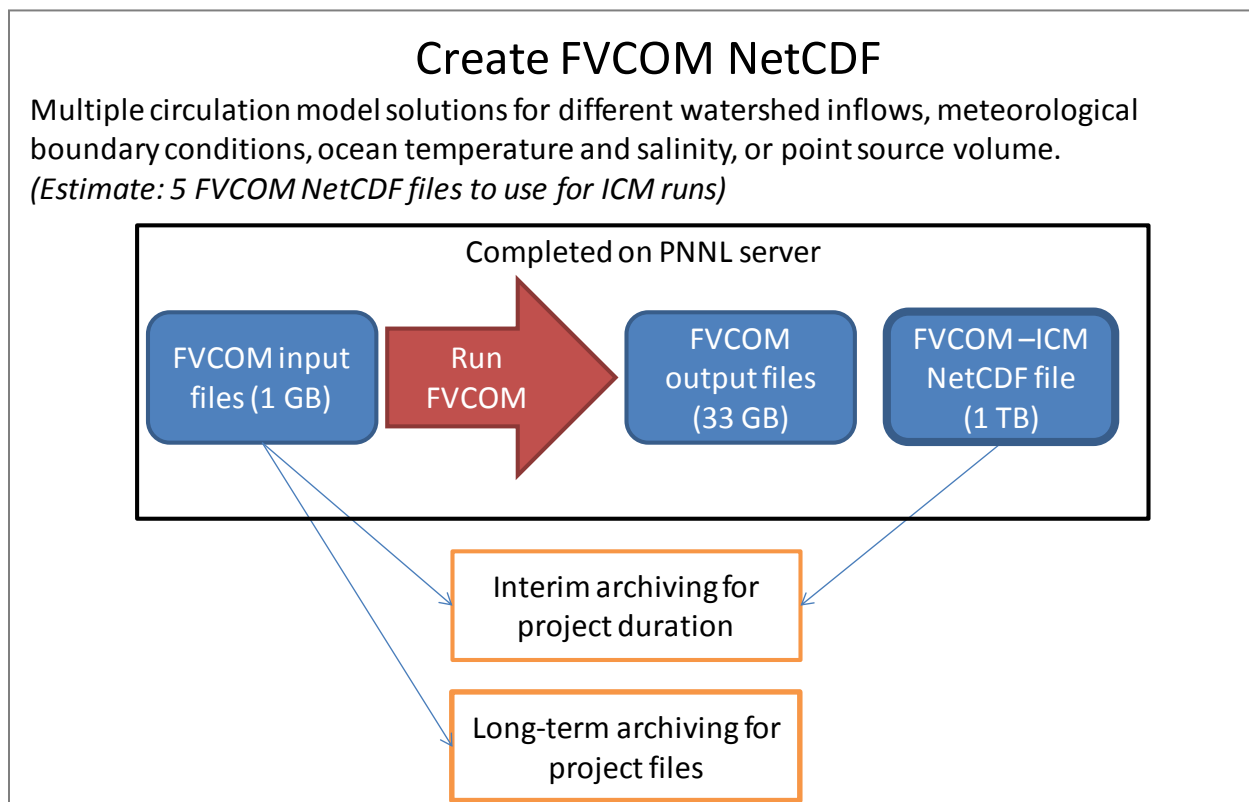
Figure 5. Process flow diagram for creating FVCOM NetCDF output.

Create ICM NetCDF

Multiple water quality model solutions for different watershed nutrients or oxygen, marine point source nutrients or oxygen, precipitation quality, ocean nutrients or oxygen.
(Estimate: 50 ICM NetCDF files to use for water quality analyses)

Completed on PNNL server

FVCOM NetCDF output file (1 TB)

ICM input files (1 GB)

Run ICM

ICM output files (22 GB)

Matlab post-processing tools

ICM NetCDF files (20 GB)

Transfer to ECY server

Interim archiving for project duration

Long-term archiving for project files

Create ICM NetCDF

Multiple water quality model solutions for different watershed nutrients or oxygen, marine point source nutrients or oxygen, precipitation quality, ocean nutrients or oxygen.
(Estimate: 50 ICM NetCDF files to use for water quality analyses)

Completed on ECY server

ICM NetCDF files (20 GB)

Matlab post-processing tools

ICM binders (30 GB)

DO plots, CFD (___ GB)

DO inventory by region (1 MB)

Other visualization tools?

Model team graphics

ArcGIS plots

Maps of DO inventory for report (1 MB)

Interim archiving for project duration

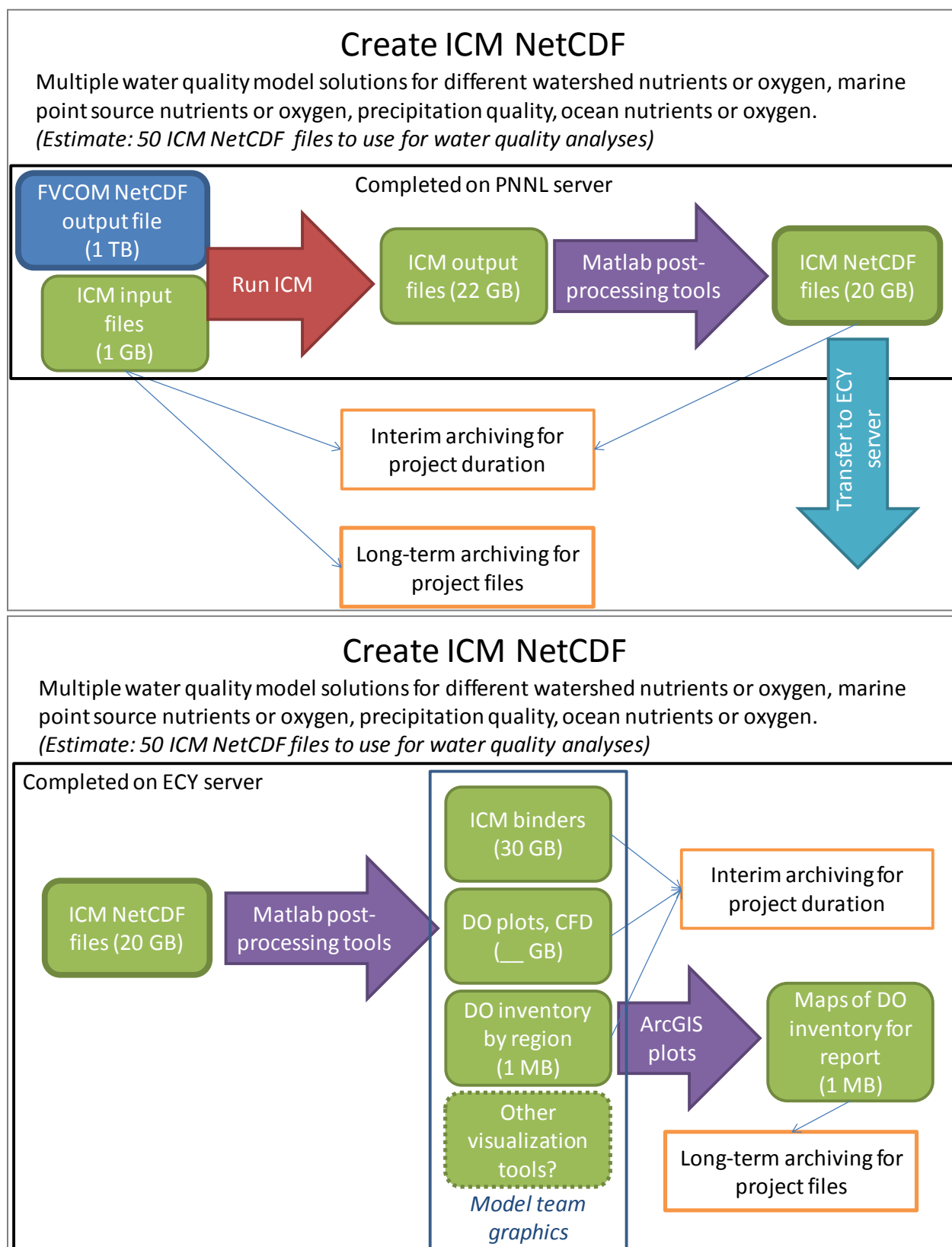Long-term archiving for project files

Figure 6. Process flow diagram for creating ICM NetCDF output.

Option 1 – Repair Existing Server

Seven of 22 compute nodes failed on the existing server in 2013 and have not yet been replaced. The cost to repair the existing server includes $3,000 for Silicon Mechanics to send a team to PNNL to conduct the installation and repairs plus $2,500 per failed node. If all seven failed nodes are replaced, the cost is $20,500 for the full repair. Another option is to replace only four of the compute nodes and use half the cluster. This would cost $13,000 to extend the working life of the server for the duration of this project.

Option 2 – Purchase New Server

Servers typically have a working life of 5 years, after which the components are more prone to failure and significant maintenance is required. A new server could replace the existing server, which would cost $95,000 to match specifications (February 2014). Additional time would be needed to set up and maintain the server. A new server could be hosted at either PNNL or at Ecology.

Hosting at PNNL has the advantage of PNNL's extensive computing environment experience and expertise. Disadvantages include the need for an ongoing contract to pay for maintenance and management of the server plus to ensure access for Ecology and others outside of PNNL. Hosting at PNNL also has the disadvantage of requiring access permission from PNNL.

Hosting at Ecology has the advantage of maintaining the equipment where Ecology has an institutional responsibility. The disadvantages include the lack of technical support for Linux-based servers. Another disadvantage is that Ecology's IT services do not support non-Windows operating systems. This would also require that Ecology's modelers maintain the server. Ecology would need to manage VPN access to the server for third parties.

Option 3 – Cloud Computing

Cloud computing offers an alternative to servers hosted at PNNL or Ecology. Cloud computing uses remote servers accessed through an internet connection, a local area network, or wide area network. Model managers set up the cloud hosting environment through a commercial provider such as Amazon, Microsoft, or Google. Cloud computing can be used to transfer initial files, set up model applications, run the model, post-process the results, and transfer final results to model users. Model managers partition the cloud computing environment to distinguish active model development requiring permission to access from information accessible to a broader set of end users. Third parties can access the cloud using pay-as-you-go accounts to transfer the output or to access the working model itself.

The Chesapeake Bay Program recently conducted a pilot application using Amazon Web Services. Results indicate that commercial cloud service providers reduced costs compared with internal hosting, cloud hosting is technically viable for the needs of the Chesapeake Bay Program, and cloud hosting improves the security, auditability, and governance of several

systems in use at the Chesapeake Bay Program (Booz Allen Hamilton, 2013). Chesapeake Bay Program migrated to cloud hosting in fall 2013.

PNNL has continued model development and application using the Department of Energy's cloud hosting services in Richland. This required internal PNNL funds to support the work but is not a long-term solution for the Salish Sea Model because access is limited.

Microsoft has developed Azure, its cloud computing platform. We will also explore options to partner with Microsoft Research for this project to assess performance.

Amazon's cloud services are in broad use. We estimate a cost of $43,000 per year to completely transition to Amazon cloud computing using the current cluster CPUs and storage space. The bulk of the costs are associated with stored data and hourly scans to archive changes to backup. This estimate is based on monthly averages of data transferred to Ecology or PNNL desktops during previous project phases. This is equivalent to 8 CPU head nodes (16 GB RAM); 172 ECU (equivalent of child nodes); and 15 TB of storage. Advantages include Ecology has an existing account and that the Chesapeake Bay Program has vetted similar needs related to accessibility and reliability of the service.

Other commercial cloud computing options exist in addition to Microsoft's Azure and Amazon's Web Services.

The following steps would be needed to run the Salish Sea Model on a cloud computing platform, with process steps presented in Figure 7:

1. Set up the environment and libraries as needed with account access for 3 Ecology users and 3 PNNL users.

2. Transfer files to the cloud

3. Apply the models, post-process the output, assess the results quantitatively and qualitatively, and define subsequent model runs.

4. Transfer final model output to Ecology and PNNL for final graphics and animations.
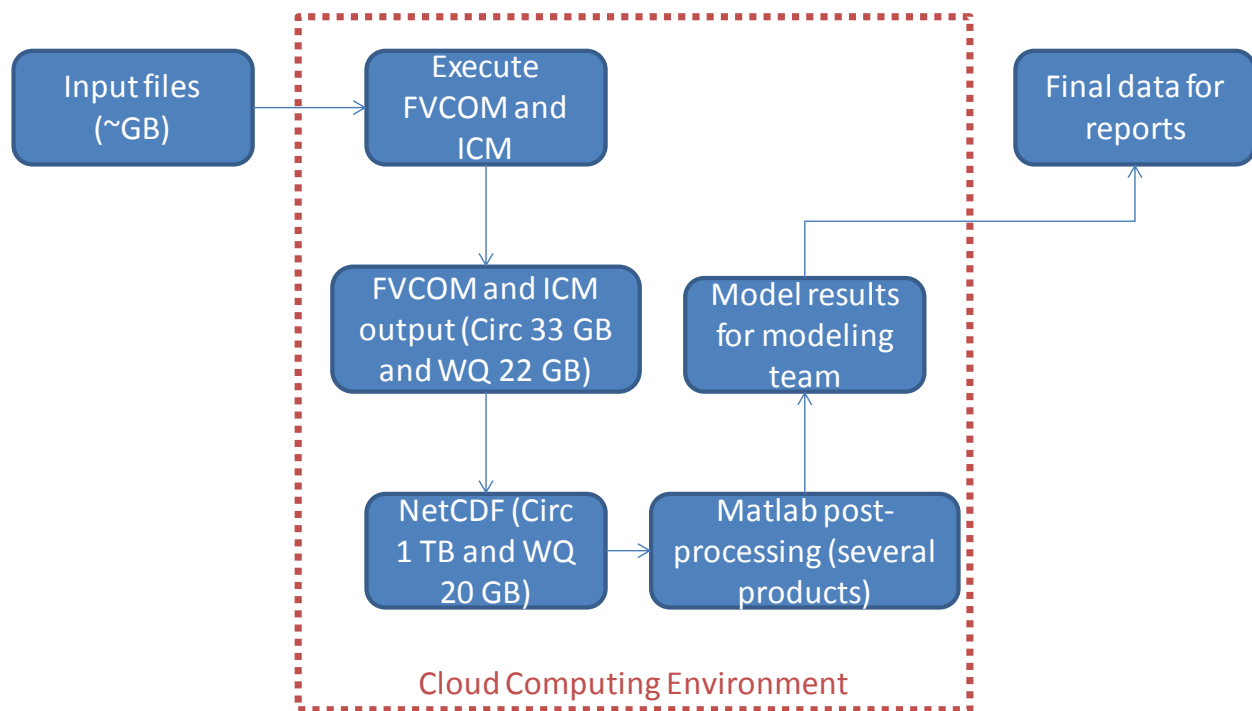
Figure 7. FVCOM-ICM process flow diagram in a cloud computing environment.

Cloud computing offers several advantages to the Salish Sea Model:

- Third parties can access model results and manipulate the models to run alternative scenarios with pay-as-you-go user accounts
- Cloud computing does not require server hardware maintenance

Disadvantages include the following:

- Difficult to predict costs during more intense model calibration periods and less intense model application periods.
- Potential 20-30% increase in runtime compared with the current servers.

Recommended Computational Platform for Sediment Diagenesis and FVCOM-ICM Model Development

We recommend repairing the existing server (replacing 7 nodes) and conducting a pilot application using Amazon Web Services cloud computing platforms (operating system, programming language, database, and web server). Department of Ecology can use a state master contract through the Department of Enterprise Services for this pilot application. We will also explore whether we can pilot the application using Microsoft's Azure cloud computing

platforms; however, we do not have an existing contract. The Amazon Web Services pilot will be conducted in parallel with initial model code changes and testing.

1. PNNL sets up the FVCOM-ICM environment with Fortran and NetCDF libraries
2. PNNL sets up a Unix environment., MPI libraries, with the ability to submit jobs with parallel processing
3. PNNL sets up and benchmarks performance tests for both the FVCOM and ICM model components of the existing Salish application.
4. PNNL summarizes the results of the tests in the same memorandum compiling results of the software code changes and testing results and submits to Ecology for review and discussion

The project team will evaluate the benchmark tests, discuss pros and cons of migrating additional application to one or both cloud computing platforms, and implement the change.

PNNL and Ecology will document the server-based and cloud-based computing approaches as an appendix to the final report.

Sampling Procedures

Not applicable; no sampling is planned.

Measurement Procedures

Not applicable; no sampling is planned.

Quality Control Procedures

Field

Not applicable; no sampling is planned.

Laboratory

Not applicable; no sampling is planned.

Data Management Procedures

Not applicable; no sampling is planned. See Model Information Management Procedures for model-related data management procedures.

Data Verification and Validation

Not applicable; no sampling is planned. See Model Calibration and Evaluation for model-related verification and validation.

Data Quality (Usability) Assessment

Not applicable; no sampling is planned. See Model Quality Usability Assessment for model-related usability assessment.

Model Setup

Once the model code changes have been made and tested against idealized conditions as described under Model Development and Testing, we will apply the model to dynamic conditions. We will use the same 2006 and 2007 boundary conditions developed and described in Khangaonkar et al. (2012 a,b) and Roberts et al. (2014) for the ocean boundary, meteorology, river inputs, and marine point sources. Water column initial conditions will use the same approach as described in Khangaonkar et al. (2012 a,b).

Limited available data exist to compare predicted fluxes to and from the sediments and sediment POC/PON with observations. Norton (2009) and Gries and Osterberg (2011) present the most recent estimates of particle fluxes for shallow and deep waters of Puget Sound. Sheibley and Paulson (2014) present a summary of available Puget Sound benthic flux data. To the extent possible, the observed fluxes will be compared with model predictions of sediment fluxes and sediment concentrations. Due to the sparse observed data and possible low bias of observed fluxes, the predicted fluxes will not be expected to exactly match the observed data, though the observed data will be used as a guide to approximately constrain the model predictions of sediment fluxes.

Initial model setup will use the current calibration values for all water column kinetics parameters with default literature parameter values for the rate constants and kinetics parameters of the SFM. The initial default parameters for the SFM will be taken from the recommended defaults for the USEPA WASP model (Table 3). Table 3 also presents the range of values reported across several estuarine studies by DiToro (2001), the final calibration values of Testa et al. (2013), and the literature ranges summarized by Testa et al. (2013).

Most of the parameter values for the SFM are commonly accepted to be the same constant values across a large number of studies (e.g., Martin and Wool, 2013; DiToro, 2001; and Testa et al., 2013) and will not be varied during calibration process. The principle rate parameters and constants that may be derived from observed data in Puget Sound or optimized during calibration include the following:

- Solids concentration will be based on observed data from sediment cores from Puget Sound. Pelletier and Mohamedali (2009) summarized data from 87 cores and reported a median of 0.6 Kg/L and interquartile range of 0.5 – 0.86 Kg/L.

- Deep burial velocity of sediment will be based on observed data from sediment cores from Puget Sound. Pelletier and Mohamedali (2009) summarized data from 87 cores using the Pb-210 method and reported a median of 0.4 cm/yr and interquartile range of 0.17 – 0.81 cm/yr.

- Porewater diffusion coefficients will be constrained within the range of 0.0005 – 0.005 m^2/d (DiToro, 2001, Table 15.5), which is consistent with the recent calculations of Sheibley and Paulson (2014) for Puget Sound sediments.

- Denitrification velocity in layer 1 will be constrained within the range of 0.1 – 0.2 m/d per DiToro (2001).

- Denitrification velocity in layer 2 will be constrained within the range of 0.25 – 0.5 m/d per DiToro (2001).

- G class 1 POC diagenesis rates will be constrained within the range of 0.01 – 0.035 d^{-1} per Testa et al. (2013) and DiToro (2001).

- Particle mixing half-saturation constant for O2 will be constrained within the range of 2 – 4 mg/L per Testa et al. (2013).

During the recalibration process, we will evaluate sensitivity to key parameters to understand the magnitudes of responses to perturbations.

Table 3. Parameter summary for rate constants and kinetics parameters of the sediment flux model.

Name	Symbol	Units	WASP default per Martin and Wool 2013	Reported value or range across estuarine studies by DiToro 2001	Testa et al 2013	Literature range per Testa et al 2013
solids concentration in aerobic layer 1	m1	kgD/L	0.5	0.2 - 1.2	0.5	--
solids concentration in anaerobic layer 2	m2	kgD/L	0.5	0.2 - 1.2	0.5	--
bioturbation particle mixing coefficient	Dp	m^2/d	0.00006	0.6	0.00006	<1e-7 - 5e-5
pore water diffusion coefficient	Dd	m^2/d	0.0025	0.0005 - 0.005	0.0005	0.6 - 8.64
deep burial velocity	w2	m/d	6.85E-06	5.5e-6 - 2.1e-5	1.92E-05	0.02 - 1.0
thickness of sediment anaerobic layer 2	H2	m	0.1	0.1	0.1	--
Reaction velocities						
freshwater nitrification velocity	KappaNH3f	m/d	0.1313	--	--	--
saltwater nitrification velocity	KappaNH3s	m/d	0.1313	0.131	0.131	--
freshwater denitrification velocity in layer 1	KappaNO3_1f	m/d	0.1	0.1 - 0.2	--	--
saltwater denitrification velocity in layer 1	KappaNO3_1s	m/d	0.1	0.1 - 0.2	0.1 - 0.3	--
denitrfication in the anaerobic layer 2	KappaNO3_2	m/d	0.25	0.25 - 0.5	0.25	--
methane oxidation in the aerobic layer 1	KappaCH4	m/d	0.7	--	--	--
Half saturation constants						
nitrification half saturation for NH4N	KM_NH3	mgN/L	0.728	0.728	0.728	0.34 - 1.2
nitrification half saturation for O2	KM_O2_NH3	mgO2/L	0.37	0.37	0.368	0.032 - 2.0
Partitioning coefficients						
partition coefficient for NH4 in layer 1 and 2	KdNH3	L/kgD	1	1	--	--
partition coefficient for PO4 in layer 2	KdPO42	L/kgD	20	20 - 1000	50 - 100	--
freshwater factor that increases the aerobic layer partition coefficient of inorganic P	dKDPO41f	unitless	20	NA	--	--
saltwater factor that increases the aerobic layer partition coefficient of inorganic P	dKDPO41s	unitless	20	20 - 300	100 - 300	--
critical O2 concentration in layer 2 for adjustment of partition coefficient for inorganic P	O2critPO4	mgO2/L	2	2	2	--
Temperature coefficients						
temperature theta for bioturbation mixing between layers 1 and 2	ThtaDp	unitless	1.117	1.08 - 1.15	1.117	1.07 - 1.117
temperature theta for pore water diffusion between layers 1 and 2	ThtaDd	unitless	1.08	1.08 - 1.15	1.08	1.08
temperature theta for nitrification	ThtaNH3	unitless	1.123	1.123	1.123	1.076 - 1.127
temperature theta for nitrification half saturation for NH4N	ThtaKmNH3	unitless	--	1.125	--	--
temperature theta for denitrification	ThtaNO3	unitless	1.08	1.08	1.08	1.056 - 1.20
temperature theta for methane oxidation	ThtaCH4	unitless	1.079	--	--	--
Salinity thresholds						
salinity above which sulfide rather than methane is produced from C diagenesis	SALTSW	psu	1	1	--	--
salinity above which saltwater nitrification/denitrification rates are used for aerobic layer	SALTND	psu	1	1	--	--
Sulfide constants						
aerobic layer reaction velocity for dissolved sulfide oxidation	KappaH2Sd1	m/d	0.2	0.2	--	--
aerobic layer reaction velocity for particulate sulfide oxidation	KappaH2Sp1	m/d	0.4	0.4	--	--
temperature coefficient for sulfide oxidation	ThtaH2S	unitless	1.079	1.08	--	--
sulfide oxidation normalization constant for O2	KMHSO2	mgO2/L	4	4	--	--
partition coefficient for sulfide in aerobic layer 1	KdH2S1	L/kgD	100	100	--	--
partition coefficient for sulfide in anaerobic layer 2	KdH2S2	L/kgD	100	100	--	--
Fractions of G classes 1 and 2 for settling PON, POC, and POP						
fraction of class 1 pon	frpon1	unitless	0.65	0.65	0.65	--
fraction of class 2 pon	frpon2	unitless	0.25	0.25	0.25	--
fraction of class 1 poc	frpoc1	unitless	0.65	0.65	0.65	--
fraction of class 2 poc	frpoc2	unitless	0.2	0.2 - 0.25	0.2	--
fraction of class 1 pop	frpop1	unitless	0.65	0.65	0.65	--
fraction of class 2 pop	frpop2	unitless	0.2	0.2 - 0.25	0.2	--
Diagenesis rate constants for G clase 1, 2, and 3 N/C/P						
G class 1 pon mineralization	kpon1	day^-1	0.035	0.035	0.01	0.019 - 0.066
G class 2 pon mineralization	kpon2	day^-1	0.0018	0.0018	0.0018	0.0012 - 0.0088
G class 3 pon mineralization	kpon3	day^-1	0	0	0	--
G class 1 poc mineralization	kpoc1	day^-1	0.035	0.035	0.01 - 0.035	0.019 - 0.066
G class 2 poc mineralization	kpoc2	day^-1	0.0018	0.0018	0.0018	0.0012 - 0.0088
G class 3 poc mineralization	kpoc3	day^-1	0	0	0	--
G class 1 pop mineralization	kpop1	day^-1	0.035	0.035	0.01	0.019 - 0.066
G class 2 pop mineralization	kpop2	day^-1	0.0018	0.0018	0.0018	0.0012 - 0.0088
G class 3 pop mineralization	kpop3	day^-1	0	0	0	--
Temperature coefficients for G class 1, 2, and 3 mineralization						
temperature theta for G class 1 pon	ThtaPON1	unitless	1.1	1.1	1.1	1.052 - 1.166
temperature theta for G class 2 pon	ThtaPON2	unitless	1.15	1.15	1.15	1.052 - 1.166
temperature theta for G class 3 pon	ThtaPON3	unitless	1.17	--	--	--
temperature theta for G class 1 poc	ThtaPOC1	unitless	1.1	1.1	1.1	1.052 - 1.166
temperature theta for G class 2 poc	ThtaPOC2	unitless	1.15	1.15	1.15	1.052 - 1.166
temperature theta for G class 3 poc	ThtaPOC3	unitless	1.17	--	--	--
temperature theta for G class 1 pop	ThtaPOP1	unitless	1.1	1.1	1.1	1.052 - 1.166
temperature theta for G class 2 pop	ThtaPOP2	unitless	1.15	1.15	1.15	1.052 - 1.166
temperature theta for G class 3 pop	ThtaPOP3	unitless	1.17	--	--	--
Parameters for partical mixing and benthic stress						
reference G1 at which w12base = Dp / H2 at 20 degC for DiToro eqn 13.1	POC1R	mgO2/gD	0.2667	0.2667	0.2667	--
first-order decay rate constant for benthic stress (d^-1) for DiToro eqn 13.3	kBEN_STR	day^-1	0.03	0.03	0.03	--
particle mixing half-saturation constant for O2 (mgO2/L)	KM_O2_Dp	mgO2/L	4	4	2	--

Model Calibration and Evaluation

Methods Overview

Once sediment diagenesis code testing and verification are complete and it is set up for 2006-2007 conditions, we will compare predicted results against observed data collected in Puget Sound and the Straits. Skill will be assessed against both water column concentrations and available sediment flux and other data. The updated model performance will be compared against that described in Khangaonkar et al. (2012 a,b). If the updated model performs as well or better, then no further calibration will occur.

Calibration refers to the process of adjusting model parameters within physically defensible ranges until the resulting predictions give the best possible match with observed data. Model evaluation is the process used to determine whether a model and its analytical results are of sufficient quality to serve as the basis for a decision and whether the model is capable of approximating the real system of interest (EPA, 2008). Some efforts refer to this as validation, confirmation, or verification.

Model calibration is an iterative procedure that combines quantitative comparison with measured data and best professional judgment. For example, phytoplankton growth, reaeration, and BOD will be adjusted to match observed DO data. Chlorophyll a data will represent phytoplankton density and will be used to adjust algal growth, die-off, respiration, and settling. The nitrogen balance will involve adjusting nitrification and organic nitrogen hydrolysis rates, as well as uptake rates by phytoplankton.

Calibration and evaluation rely on a combination of quantitative statistics for goodness-of-fit and visual comparison of predicted and observed time series and depth profiles (Krause et al., 2005). We will use similar approaches as reported in Roberts et al. (2012) and Ahmed et al. (2014). Numeric targets for RMSE or bias are not specified. We will maximize model skill consulting EPA (2009) and the project advisory committee.

Targets and Goals

We will assess model performance using both root mean square error (RMSE) and bias for predicted and observed DO, chlorophyll a (algae), nitrate plus nitrite, and phosphate for the nine stations summarized in Table 3.4 of Khangaonkar et al. (2012 a,b). While we cannot specify the maximum tolerable values for RMSE or bias, we will compare the values with other studies and the previous calibration. Both RMSE and bias are measures of model accuracy. In addition, we will check the vertical fluxes in the bottom water layer and top sediment layer.

Performance measures include RMSE and bias for:

- Nutrient, dissolved oxygen, and chlorophyll profiles
- Nutrient, dissolved oxygen, and chlorophyll time series in the surface and bottom layers at representative stations throughout the model domain

If the model skill worsens compared with the previous calibration (Khangaonkar et al., 2012 a,b), we will recalibrate the oxygen model with the diagenesis components in place. We will follow the calibration and evaluation steps identified in Sackmann (2009) beginning with the final calibration values described in Khangaonkar et al. (2012 a,b).

The calibration period for this model application is 2006-07. As described in Sackmann (2009), several intensive monitoring programs occurred in 2006, such as the South Puget Sound Dissolved Oxygen Study (Mohamedali et al., 2011) and the Hood Canal Dissolved Oxygen Program (www.hoodcanal.washington.edu/). In addition, the Department of Ecology (www.ecy.wa.gov/programs/eap/mar_wat/index.html) and King County (green.kingcounty.gov/marine/routineMonitoring.aspx) conduct ambient monitoring programs of the marine waters of Puget Sound and the Straits.

Among the water quality parameters, calibration will focus on representing the DO concentrations well. The overall process will be to describe the bulk of the data, and short-term effects of ephemeral events may not be represented. The highest priority will be to describe the DO levels in the late-summer months, when the lowest levels are expected.

Sensitivity and Uncertainty Analyses

To evaluate model performance and the variability of results, we will perform sensitivity analyses and will analyze uncertainty. Uncertainty can arise from a number of sources that range from errors in the input data used to calibrate the model, to imprecise estimates for key parameters, to variations in how processes are parameterized in the model domain. We will assess and reduce uncertainty consistent with EPA (2009).

Sensitivity refers to how much results are affected by changes in one or more input parameters. In contrast, uncertainty analysis investigates the lack of knowledge about a certain environmental component or the real value of model parameters. Although sensitivity and uncertainty are closely related, uncertainty is parameter-specific and sensitivity is algorithm-specific with respect to model variables. By investigating the relative sensitivity of model parameters, a user can become knowledgeable of the relative importance of parameters in the model. By knowing the uncertainty associated with parameter values and the sensitivity of the model to specific parameters, a user will be more informed regarding the confidence that can be placed in the model results (EPA, 2009).

We will evaluate responsiveness of the sediment model components to various assumptions and rate constants within the new sediment module even if no overall oxygen model recalibration is needed. If recalibration is needed, we will also evaluate responsiveness of the model predictions to various assumptions and rate constants governing water column processes. Specific analyses include boundary conditions, meteorological forcing, watershed loads, and process rate parameters. We will increase or decrease parameters by a factor of 2 or an order of magnitude. The final report will document the parameters that have the greatest uncertainty and strongly influence the results, as was done in Roberts et al. (2014).

Numerous sensitivity tests of the water quality model were performed as part of the previous study calibration (Khangaonkar et al., 2012 a,b) which resulted in acceptable model calibration and selection of model coefficients for water column processes. After assessing model performance and possibly recalibrating the model, we will conduct sensitivity tests by perturbing key model parameters, including:

- Phytoplankton kinetics (maximum growth rate, optimum temperature, optimum light, nitrogen half-saturation rates, carbon-to-chlorophyll ratios, sinking rates)

- Zooplankton kinetics (grazing rate)

- Benthic processes that lead to nitrogen and dissolved oxygen flux

Model Information Management Procedures

Model Software Version Control

The primary models FVCOM and FVCOM-ICM used in this Salish Sea modeling effort are public domain research codes that undergo modification and testing as part of model development (e.g., development and incorporation of the of the sediment diagenesis kinetics into FVCOM-ICM). To ensure all users work with the most recent tested version, PNNL uses public domain version control software (e.g., SVN) to manage model files and directories over time. Files are stored in a central repository. The repository is much like an ordinary file server, except that it records every change ever made to files and directories. This allows recovery of older versions of the files and examines the history of how and when your data changed, and who changed it. The users conduct development under their own branches before committing the update to the trunk or central repository. SVN repository for this project includes model source codes, pre-processing software, post processing utilities, model application examples and test cases, and related tools and utilities.

Cluster Computer Data Management

All model runs are conducted on Ecology or PNNL high performance cluster computers housed in Seattle or Richland, WA. The model input files with the associated case names are uploaded to the cluster machines by the respective users. The model runs are conducted on these cluster machines through remote login. The models generate large volumes of data. The raw data are processed directly on the cluster computers and processed outputs are downloaded by the individual users to their personal computers for documentation. The data are also stored by each user under their own accounts on the cluster machines and periodically backed up on the 10 TB RAID data storage array.

Project Input and Output Files

Project Share and Transfer: Following the completion of each model scenario, the model input and post processed output files are posted to the project share directory on the Ecology cluster machine. Users from PNNL and Ecology are provided common access to the share directory. Solution files from this location may be downloaded by individual users for further visualization, processing, and posting on the project websites.

Modeling Project Folders

For each project, standard folders are created on the user's desktop computer under the project directory such as \Monitoring Data, \Model_Input, \Model_Output, Post Processing, References, and Reports. Under \Model_Input and \Model_Output, subfolders are created using recognizable names such as \calibration (with numerous iterations 01, 02 …). Also included are folders corresponding to model application for the scenarios.

Secondary Backup on USB Data Storage Disks

The project files, model input files, and post processed data files are also periodically backed up on external data storage devices.

Model Output Quality (Usability) Assessment

We will evaluate whether the outcomes have met the project's objectives and will summarize model performance in the final report. Criteria to be evaluated include whether or not the water quality model:

- Behaves in a manner that is consistent with the current understanding of processes known to affect water quality in the Salish Sea.

- Realistically reproduces variations in water quality observed within individual subbasins of Puget Sound and the Straits on inter-annual, seasonal, and possibly intra-seasonal timescales.

Audits, Reports, and Project Outputs (Deliverables) and Schedule

Although the project will produce a single draft and final report summarizing the results, interim results will be evaluated internally and externally as the project progresses.

The modeling team will meet approximately monthly to review recent progress, evaluate project needs, and revisit next steps to meet project objectives. This provides an internal audit function.

We will present interim results to the project advisory group at key project junctures. These meetings provide review from external parties on key graphics before extensive report writing is completed.

Finally, we will document findings in the final project report. Reports are developed consistent with Ecology's Quality Assurance program and publications guidelines. Key elements include internal review, external review by the project advisory group, and peer review. Peer review must follow strict protocols established by Ecology's Quality Assurance Program. Once reviews are complete, the publications process requires extensive documentation of the review process.

Ecology's document template requires the following elements for the final report:

- Introduction – project description, purpose

- Methods – technical approach, including a summary of sediment diagenesis

- Results – calibration results, sensitivity, uncertainty, scenarios

- Discussion – implications of the results

- Conclusions –

- Recommendations – how should this information be used?

- References – all cited sources

- Appendices – technical background as needed such as model code changes or model parameter values; glossary, acronyms, abbreviations, units of measurement

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Appendices

Appendix A. Detailed Description of Sediment Diagenesis Model

Introduction

The basic framework of the sediment model consists of two well-mixed sediment layers, underlying each surface water column segment: a thin upper sediment layer (the aerobic layer) and a thicker active (anaerobic) layer (Figure A-1). In WASP, the thickness of the active layer is specified by the user (input) and assumed constant among all sediment columns. Three major processes included in the sediment model are the:

- Fluxes of particulate organic matter from the water column to the sediments (note that since the upper sediment layer is assumed to have a negligible thickness, the fluxes are deposited directly into the second, or anaerobic layer),
- Mineralization (or diagenesis) of the particulate organic matter, and
- Reactions and transfers (between sediment layers, to the water column and deep inactive sediments) of the reaction products.
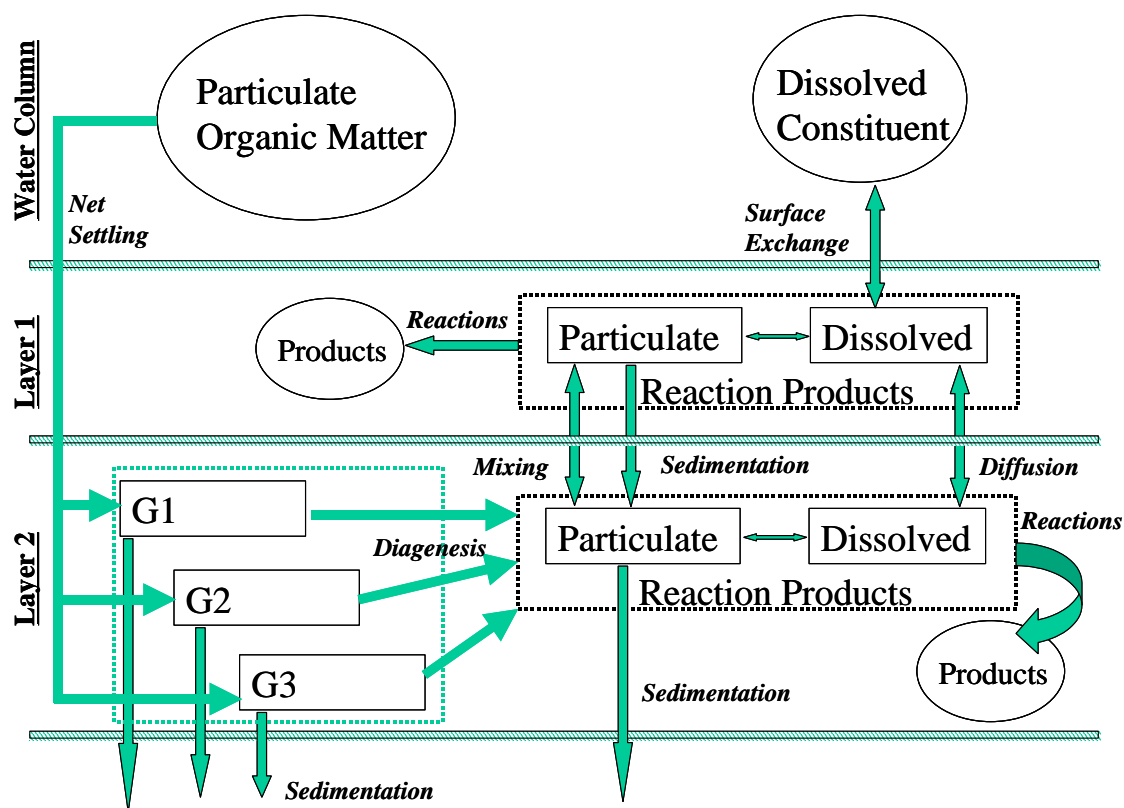

Figure 0-1

Figure A-1. Sediment model framework.

Particulate Organic Matter Fluxes (Deposition)

Fluxes of particulate organic matter (POM) from the water column represent a source term for the sediments. The particulate organic matter fluxes are subdivided into particulate organic carbon (C, in oxygen equivalents), nitrogen (N) and phosphorus forms (POC, PON and POP) and then into separate forms (G-classes) based upon their reactivity.

The flux of POM from the water column to the sediments is computed using the standard WASP transport conventions for the following state variables: CBOD, algae, organic nitrogen and organic phosphorus. In WASP, settling fluxes for these state variables are computed based upon the specified fraction dissolved (which can vary by segment and state variable), specified particulate transport field (for the state variable) and the specified rates of solids transport (flow fields 1 to 3). The particulate organic carbon, in the diagenesis model, is in oxygen equivalent units (CBOD) as opposed to carbon units in similar models. The flux of algae to the sediment model is subdivided into carbon (oxygen equivalents), nitrogen and phosphorus using specified stoichiometric constants.

Internal sediment state variables for diagenesis are based upon the multi-class G model, in which the organic forms are divided based upon their reactivity into reactive (G1), refractory (G2), and inert (G3) forms (**Error! Reference source not found.**). Therefore the fluxes of particulate organic carbon (oxygen equivalents), nitrogen, and phosphorus are subdivided into G-class fractions, based upon user specified ratios. Due to the negligible thickness of the upper layer, deposition (as described later) is assumed to proceed directly from the water column to the lower (anoxic) sediment layer.

Diagenesis

Diagenesis reactions are assumed to occur in the second (anaerobic) sediment layer. The diagenesis equations are solved for each form of particulate organic matter (POM; forms for N, P and C where C is in oxygen equivalents) and for each G class (1-3) using the same basic formulation. In order to compute the time-varying diagenesis for each modeled variable, a mass balance equation is written as

Equation 1

$$\frac{\partial C_{T2}}{\partial t} = \frac{J_2}{H_2} - \frac{W_2}{H_2} C_{T2}^{t+\Delta t} - K_2 C_{T2}^{t+\Delta t} \approx \frac{C_{T2}^{t+\Delta t} - C_{T2}^t}{\Delta t}$$

where

$C_{T2}^{t+\Delta t}$ = total concentration in layer 2 at time t+Δt
C_{T2}^t = total concentration in layer 2 at time t (from initial conditions or computed value from previous time step)

Δt   = time step (from the water quality model converted to internal units)
J_2 = flux from the water column,
H_2 = thickness of the active sediment layer (input variable),
K_2 = reaction velocity (specific to chemical and G class, temperature corrected), and

W_2 = net sedimentation velocity (input variable)

The mass balance equation is solved algebraically for the concentration at the present time step, as

Equation 2

$$C_{T2}^{t+\Delta t} = \frac{J_2 \dfrac{\Delta t}{H_2} + C_{T2}^t}{1 + K_2 H_2 \dfrac{\Delta t}{H_2} + W_2 \dfrac{\Delta t}{H_2}}$$

Once the concentrations at the present time step are computed, the diagenesis source terms for reactions and transfers ($J_{T2}^{t+\Delta t}$) are computed. Diagenesis source terms are computed for C, N and P from the sum of the product of the chemical specific reaction velocities (K_2) and computed concentrations in each of the three G classes. For example,

Equation 3

$$J_{T2}^{t+\Delta t} = \sum_{i=1}^{3} K_{2,i} C_{T2,i}^{t+\Delta t}$$

where

$J_{T2}^{t+\Delta t}$	=	source term for total chemical in layer 2 at time t+Δt
K2,i	=	reaction velocity for total chemical in G class i
$C_{T2,i}^{t+\Delta t}$	=	total chemical concentration for G class i

The WASP diagenesis model also contains an option for steady-state computations for use in computing the initial conditions for the model. The steady-state computations involve an iterative solution for kinetic reactions, as discussed in a following section. That is, an initial guess for the solution is specified (the initial conditions) and the computations iterated until the solution converges. The maximum number of allowable iterations and convergence criteria are specified in input. For POM diagenesis, the steady-state solution to Equation 1 is given by

Equation 4

$$C_{T2} = \frac{\dfrac{J_2}{H_2}}{K_2 + \dfrac{W_2}{H_2}}$$

Reactions and Transfers

Overview

Once the sediment particulate organic matter (C, N and P) concentrations and source terms are computed for the present time step, as described above, the reactions and transfers are computed. Concentrations of ammonia, nitrates, methane, sulfides, silica and phosphorus are computed, and then used to compute fluxes to the overlying water column.

The total chemical concentrations are computed from mass balance relationships for each of the two sediment layers. Since the surface layer is thin (on the order of 0.1 cm) compared to the active anaerobic layer (on the order of 10 cm), it is assumed that layer 1 can be considered at steady-state in comparison to the slower processes occurring in layer 2. From DiToro (2001; Equations 13.28 and 13.30), the two equations solved are

Layer 1

Equation 5

$$0 = -s\left(f_{d1}C_{T1}^{t+\Delta t} - C_{dO}^{t+\Delta t}\right) + \omega_{12}\left(f_{p2}C_{T2}^{t+\Delta t} - f_{p1}C_{T1}^{t+\Delta t}\right) + K_{L12}\left(f_{d2}C_{T2}^{t+\Delta t} - f_{d1}C_{T1}^{t+\Delta t}\right)$$

$$-\omega_2\,C_{T1}^{t+\Delta t} - \frac{\kappa_1^2}{s}C_{T1}^{t+\Delta t} + J_{T1}^{t+\Delta t} + C_{T2}^{t+\Delta t}\,\overset{\bullet}{H_1^{+}} - C_{T1}^{t+\Delta t}\left(\overset{\bullet}{H_1} + \overset{\bullet}{H_1^{-}}\right)$$

Layer 2

Equation 6

$$0 = -\omega_{12}\left(f_{p2}C_{T2}^{t+\Delta t} - f_{p1}C_{T1}^{t+\Delta t}\right) - K_{L12}\left(f_{d2}C_{T2}^{t+\Delta t} - f_{d1}C_{T1}^{t+\Delta t}\right) - \kappa_2 C_{T2}^{t+\Delta t} + \omega_2(C_{T1}^{t+\Delta t} - C_{T2}^{t+\Delta t})$$

$$-\frac{H_2 C_{T2}^{t+\Delta t}}{\Delta t} + J_{T2}^{t+\Delta t} + \frac{H_2 C_{T2}^{t}}{\Delta t} + C_{T2}^{t+\Delta t}\,\overset{\bullet}{H_1^{+}} - C_{T2}^{t+\Delta t}\left(\overset{\bullet}{H_2} + \overset{\bullet}{H_1^{+}}\right)$$

s = surface transfer rate; SOD/[$O_2(0)$], where SOD=SOD rate and $O_2(0)$ is the overlying water concentration
f_{d1} = fraction dissolved in layer 1
f_{d2} = fraction dissolved in layer 2
f_{p1} = fraction particulate in layer 1
f_{p2} = fraction particulate in layer 2
$C_{T1}^{t+\Delta t}$ = total concentration in layer 1 at time t+Δt
$C_{T2}^{t+\Delta t}$ = total concentration in layer 2 at time t+Δt
C_{T2}^{t} = total concentration in layer 2 at time t
$C_{dO}^{t+\Delta t}$ = concentration in overlying water column
K_{L12} = mass transfer coefficient via diffusion
ω_{12} = particle mixing coefficient between layers 1 and 2
ω_2 = sedimentation velocity for layer 2
$J_{T1}^{t+\Delta t}$ = source term for total chemical in layer 1 at time t+Δt
$J_{T2}^{t+\Delta t}$ = source term for total chemical in layer 2 at time t+Δt
κ_1^2 = square of reaction velocity in layer 1
κ_2 = reaction velocity in layer 2

$\overset{\bullet}{H_1^{-}}$ = time derivative for H in layer 1 (*not used*)

$\overset{\bullet}{H_1^{+}}$ = time derivative for H in layer 1 (*not used*)

$\overset{\bullet}{H_1}$ = time derivative for H in layer 1 (*not used*)

$\overset{\bullet}{H_2}$ = time derivative for H in layer 2 (*not used*)

H_2 = thickness of layer 2

Δt = time step

The two equations and two unknowns can be written in the form

Equation 7

$$a_{11}x_1 + a_{12}x_2 = b_1$$

Equation 8

$$a_{21}x_1 + a_{22}x_2 = b_2$$

The equations are solved for the new concentrations ($C_{T1}{}^{t+\Delta t}$ and $C_{T2}{}^{t+\Delta t}$) using a matrix. The solution to this system of equations is (Chapra and Canale 1998) as follows:

$$x_1 = \frac{a_{22}b_1 - a_{12}b_2}{a_{11}a_{22} - a_{12}a_{21}}$$

$$x_2 = \frac{a_{11}b_2 - a_{21}b_1}{a_{11}a_{22} - a_{12}a_{21}}$$

where the elements of the matrix are:

Equation 9

$$a_{11} = -s(f_{d1}) - \omega_{12}(f_{p1}) - K_{L12}(f_{d1}) - \omega_2 - \frac{\kappa_1^2}{s}$$

Equation 10

$$a_{21} = +\omega_{12}(f_{p1}) + K_{L12}(f_{d1}) + \omega_2$$

Equation 11

$$a_{12} = +\omega_{12}(f_{p2}) + K_{L12}(f_{d2})$$

Equation 12

$$a_{22} = -\omega_{12}(f_{p2}) - K_{L12}(f_{d2}) - \kappa_2 - \omega_2 - \frac{H_2}{\Delta t}$$

Equation 13

$$b_1 = -J_{T1}^{t+\Delta t}$$

Equation 14

$$b_2 = -J_{T2}^{t+\Delta t} - \frac{H_2 C_{T2}^{t}}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 15

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \kappa_2 - \omega_2$$

Equation 16

$$b_2 = -J_{T2}^{t+\Delta t}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 17

$$f_{d,1} = \frac{1}{1+\pi_{C1}S_1}; f_{p,1} = \frac{\pi_{C1}S_1}{1+\pi_{C1}S_1}$$

$$f_{d,2} = \frac{1}{1+\pi_{C2}S_2}; f_{p,2} = \frac{\pi_{C2}S_2}{1+\pi_{C2}S_2}$$

where

π_{C1} = partition coefficient for total chemical in layer 1
π_{C2} = partition coefficient for total chemical in layer 2
S_1 = solids concentration in layer 1
S_2 = solids concentration in layer 2

The equations are conveniently solved for the new concentrations ($C_{T1}^{t+\Delta t}$ and $C_{T2}^{t+\Delta t}$) using the matrix solution. Once the concentrations have been updated, the flux of the material to the overlying water column (J) can be computed from:

Equation 18

$$J = s\left(f_{d1}C_{T1}^{t+\Delta t} - C_{dO}^{t+\Delta t}\right)$$

The surface transfer rate (s) quantifies the mixing between layer 1 and the overlying water column, which can be related to sediment oxygen demand by (Di Toro 2001).

Equation 19

$$SOD = D\frac{d[O_2]}{dz}\bigg|_{z=0} \approx D\frac{[O_2(0)-O_2(H_1)]}{H_1} = \frac{D}{H_1}[O_2(0)]$$

where
D = rate of oxygen diffusion
$O_2(0)$ = oxygen concentration of the overlying water, and
$O_2(H_1)$ = oxygen concentration at the depth H_1

assuming a straight line approximation of the derivative, so that the mass transfer coefficient ($K_{L,O2}$) may be estimated from (Di Toro 2001)

Equation 20

$$K_{L,O2} = \frac{D}{H_1} = \frac{SOD}{[O_2(o)]} = s$$

The reaction rate in the aerobic layer is formulated as a first order rate (K_1), where the term in the layer 1 equation is K_1H_1. The depth of the aerobic zone follows the definition of the surface mass transfer coefficient ($s=D/H_1$) so that $K_1H_1=K_1D_1/s$ so that

Equation 21

$$\kappa_1 = \sqrt{DK_1}$$

and

Equation 22

$$K_1H_1 = \frac{\kappa_1^2}{s}$$

which is the term applied to the total chemical in the equation for layer 1 (Equation 5). The rate of mixing of the sediment by macrobenthos (bioturbation, w_{12}) is estimated by an apparent particle diffusion coefficient (D_p), temperature corrected that varies with the biomass of the benthos. Assuming that the mass of the benthos is proportional to the labile carbon in the sediment ($C_{POC,1}^t$, or POC, in oxygen equivalents in layer 2 in G class 1),

Equation 23

$$w_{12}^* = D_P \frac{\Theta^{(T-20)}}{H_2/2} \frac{C_{POC,1}^t}{C_{POC,R}}$$

where w_{12}^* is a particle mixing coefficient that is further modified as discussed below and $C_{POC,R}$ is a reference POC concentration. Note that in the above equation and elsewhere, POC in the WASP code is in units of oxygen equivalents. Also note that the ICM code and Equation 13.1 of DiToro (2001) use H_2 in denominator, rather than $H_2/2$, so that the user should use caution in providing the appropriate value for D_p when comparing model codes or inputs.

An additional impact is that if anoxia occurs for periods of time, the benthic population is ultimately reduced or eliminated, so that bioturbuation is consequently reduced or eliminated. To include this effect, Di Toro (2001) computes the stress that low dissolved oxygen conditions (benthic stress, S) imposes on the population assuming that the stress accumulates as

Equation 24

$$\frac{\partial S}{\partial t} = -k_s S^{t+\Delta t} + \frac{K_{M,D_P}}{K_{M,D_P} + [O_2(0)]} \approx \frac{S^{t+\Delta t} - S^t}{\Delta t}$$

where
ks = decay constant for benthic stress,
$K_{M,Dp}$ = particle mixing half-saturation concentration for oxygen
which can be solved for

Equation 25

$$S^{t+\Delta t} = \frac{S^t + \dfrac{K_{M,D_P}}{K_{M,D_P} + [O_2(0)]}\Delta t}{1 + k_s \Delta t}$$

As $[O_2(0)]$ approaches zero, then $(1-k_sS)$ approaches zero, so that the particle mixing coefficient is similarly reduced, as

Equation 26

$$w_{12} = w_{12}^* \left(1 - k_s S^{t+\Delta t}\right)$$

The stress is continued at the minimum value for the year to conform with the observation that once the benthic population has been reduced by low dissolved oxygen, it does not recover until the next year (Di Toro 2001).

The dissolved phase mixing coefficient between layers 1 and 2 (K_{L12}) is due to passive molecular diffusion that is enhanced by the action of organisms (bio-irrigation). The mixing coefficient is computed from (Equation 13.6, Di Torro 2001)

Equation 27

$$K_{L12} = \frac{D_D}{H_2/2}\Theta^{(T-20)}$$

where
D_D =   pore-water diffusion coefficient
$K_{L,B}$ =   ratio of bio-irrigation to bio-particle mixing.

Note that the ICM code uses H_2 in denominator, rather than $H_2/2$, so that the user should use caution in providing the appropriate value for D_D when comparing model codes or inputs. The sediment temperature is assumed equal to the temperature of the overlying water column.

The solution of the reaction and transfer equations comprises the bulk of the computations of the diagenesis model. Part of the complexity results from the relationship of the surface transfer coefficient (s) to the sediment oxygen demand (SOD) and dissolved oxygen concentration in the overlying water column $\{O_2(0); s=SOD/[O_2(0)]\}$. Since the SOD is a function of the computed ammonia, nitrate (denitrification), sulfide (salt water) or methane (fresh water) concentrations, an iterative solution is required for those constituents. The procedure for the solution is:

1. Start with an initial estimate of the SOD
2. Solve layer 1 and 2 equations for ammonia, nitrate, sulfide and methane
   a. Solve for the ammonia flux by establishing the chemical specific conditions
   b. Compute the oxygen consumed by nitrification (NCOD)
   c. Solve for the nitrate flux by establishing the chemical specific conditions

d. Compute methane (fresh water) or sulfide (salt water) oxidation
　　　　　　i. For salt water, compute sulfide reaction terms and compute SOD due to hydrogen sulfide
　　　　　　ii. For fresh water, compute methane flux by establishing the chemical specific
　　　　　　　　1. Compare computed and saturation concentrations and correct
　　　　　　　　2. Calculate the CSOD due to methane
　　　　a. Compute the total CSOD due to sulfides or methane
　　　　b. Compute flux terms
　　　　c. Compute the total SOD due to the sulfide or methane, adding term for NCOD
　　　　d. Refine the estimate of SOD. A root finding method is used to make the new estimate
　　3. Go to step (2) if no convergence

Once the SOD is determined, then the layer 1 and 2 equations for phosphate and silica can be solved and the flux rates determined.

Computation of SOD and related reactions

As discussed above, the SOD is computed iteratively using a function Zbrent from Numerical Recipes, Press et al. (1992), which finds the root of a function without knowing the derivative. The SOD related terms are solved for each iteration, until convergence is attained. The computations require the solution of equations for ammonia, nitrate, nitrite, sulfide (salt water) or methane (fresh water) reactions, along with the carbonaceous and nitrogeneous SOD. The computation of each of these terms is briefly presented below.

Ammonia

The two-layer mass balance equations for ammonia are:

Layer 1
Equation 28

$$0 = -s\left(f_{d1}C_{NH4T,1}^{t+\Delta t} - C_{NH4T,O}^{t+\Delta t}\right) + \omega_{12}\left(f_{p2}C_{NH4T,2}^{t+\Delta t} - f_{p1}C_{NH4T,1}^{t+\Delta t}\right)$$

$$+ K_{L12}\left(f_{d2}C_{NH4T,2}^{t+\Delta t} - f_{d1}C_{NH4T,1}^{t+\Delta t}\right) - \omega_2\, C_{NH4T,1}^{t+\Delta t} - \frac{\kappa_{NH4,1}^2\,\theta^{T-20}}{s}\,f_O f_{NH4}\, f_{d1}C_{NH4T,1}^{t+\Delta t}$$

Layer 2
Equation 29

$$0 = -\omega_{12}\left(f_{p2}C_{NH4T,2}^{t+\Delta t} - f_{p1}C_{NH4T,1}^{t+\Delta t}\right) - K_{L12}\left(f_{d2}C_{NH4T,2}^{t+\Delta t} - f_{d1}C_{NH4T,1}^{t+\Delta t}\right)$$

$$+ \omega_2(C_{NH4T,1}^{t+\Delta t} - C_{NH4T,2}^{t+\Delta t}) - \frac{H_2 C_{NH4T,2}^{t+\Delta t}}{\Delta t} + J_{NH4T,2}^{t+\Delta t} + \frac{H_2 C_{NH4T,2}^{t}}{\Delta t}$$

where all terms have been previously defined, with the exception of two terms for the surface layer (f_{NH4}, f_O). Note that the primary difference between the general equations presented previously and the ammonia equations are that the square of the reaction velocity in layer 1 (nitrification) is applied only to the dissolved fraction and is modified by functions based on the oxygen and ammonia concentrations. Note also that there are two separate reaction velocities that may be specified for layer 1 in the diagenesis code ($\kappa_{NH4,1}$), for fresh and salt waters respectively, with the one used based on the salinity (SAL) of the overlying water column as compared to a salinity switch (input). In addition, the reaction velocity for layer 2 is zero. The source term for ammonia in layer 2 is equal to the flux from the diagenesis of PON.

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 30

$$a_{11} = -\left(f_{d1}\right)K_{L12} - \left(f_{p1}\right)\omega_{12} - \frac{\kappa_{NH4}^2 \theta^{T-20}}{s}\, \mathbf{f_O}\, \mathbf{f_{NH4}}\, f_{d1} - \left(f_{d1}\right)s - \omega_2$$

Equation 31

$$a_{21} = +\omega_{12}\left(f_{p1}\right) + K_{L12}\left(f_{d1}\right) + \omega_2$$

Equation 32

$$a_{12} = +\omega_{12}\left(f_{p2}\right) + K_{L12}\left(f_{d2}\right)$$

Equation 33

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2 - \frac{H_2}{\Delta t}$$

Equation 34

$$b_1 = -s\, C_{NH4T,O}^{t+\Delta t}$$

Equation 35

$$b_2 = -J_{NH4T,2}^{t+\Delta t} - \frac{H_2 C_{NH4T,2}^t}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 36

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2$$

Equation 37

$$b_2 = -J_{NH4T,2}^{t+\Delta t}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 38

$$f_{d1} = \frac{1}{1 + \pi_{NH4} S_1}; f_{p1} = \frac{\pi_{NH4} S_1}{1 + \pi_{NH4} S_1}$$

$$f_{d2} = \frac{1}{1 + \pi_{NH4} S_2}; f_{p1} = \frac{\pi_{NH4} S_2}{1 + \pi_{NH4} S_2}$$

where

π_{NH4} = partition coefficient for ammonia
S_1 = solids concentration in layer 1
S_2 = solids concentration in layer 2

The modification of the nitrification reaction for dissolved oxygen is computed from

Equation 39

$$f_O = \frac{O_{2,0}}{O_{2,0} + K_{NH4,O2}}$$

where

$O_{2,0}$ = dissolved oxygen concentration in the overlying water column, and
$K_{NH4,O2}$ = half-saturation concentration of dissolved oxygen in the nitrification reaction

The modification for ammonia concentrations is computed by

Equation 40

$$f_{NH4} = \frac{K_{NH4}}{C_{NH4,1}^t + K_{NH4}}$$

where

$C_{NH4,1}^t$ = ammonia concentration from the previous time step,
K_{NH4} = half-saturation concentration of ammonia in the nitrification reaction

Note that if K_{NH4} is specified in input, the f_{NH4} is computed as above. Otherwise $f_{NH4}=1$. Once the ammonia concentrations have been updated, the flux to the water column is computed from:
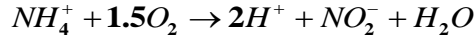
Equation 41

$$J_{NH4} = s\left(C_{NH4,1}^{t+\Delta t} - C_{NH4,0}\right)$$

where J_{NH4} is the flux to the water column.

In order to compute the oxygen consumption due to the oxidation of ammonia in the aerobic layer, the two-stage reaction can be represented by (Chapra 1997, Di Toro 2001)

Equation 42

$$NH_4^+ + \mathbf{1.5}O_2 \rightarrow \mathbf{2}H^+ + NO_2^- + H_2O$$

so that the consumption of oxygen during the process can be represented by (Chapra 1997, Equation 23.3)

Equation 43

$$a_{no} = \frac{\mathbf{1.5(32)}}{\mathbf{14}} = \mathbf{3.43} \quad gO \quad gN^{-1}$$

Therefore the contribution of the oxidation of ammonia to SOD can be estimated from

Equation 44

$$NSOD_{NH_4} = a_{no} \frac{\kappa_{NH4,1}^2 \theta^{T-20}}{s} f_O f_{NH4} \; f_{d1} C_{NH_4,1}^{t+\Delta t}$$

Nitrite

The two-layer mass balance equations for nitrite are:

Layer 1

Equation 45

$$0 = -s\left(C_{NO2,1}^{t+\Delta t} - C_{NO2,O}^{t+\Delta t}\right) + K_{L12}\left(C_{NO2,2}^{t+\Delta t} - C_{NO2,1}^{t+\Delta t}\right) - \omega_2 \; C_{NO2T,1}^{t+\Delta t}$$

$$-\frac{\kappa_{N02,1}^2 \theta^{T-20}}{s} f_O C_{NO2,1}^{t+\Delta t} + \frac{\kappa_{NH4,1}^2 \theta^{T-20}}{s} f_O f_{NH4} \; f_{d1} C_{NH_4,1}^{t+\Delta t}$$

Layer 2

Equation 46

$$0 = -K_{L12}\left(C_{NO2,2}^{t+\Delta t} - C_{NO2,1}^{t+\Delta t}\right)$$

$$+\omega_2 (C_{NO2,1}^{t+\Delta t} - C_{NO2,2}^{t+\Delta t}) - \frac{H_2 C_{NO2,2}^{t+\Delta t}}{\Delta t} + \frac{H_2 C_{NO2,2}^t}{\Delta t}$$

where all terms have been previously defined. Note that the primary difference between the general equations presented previously and the nitrite equations are that

- The reaction velocity for nitrite is modified by the dissolved oxygen concentration in the overlying water column (factor f_O)

- All nitrite is assumed dissolved, therefore the fraction particulate is zero and the rate of particle mixing zero
- The first-stage nitrification loss from layer one becomes a source term for nitrite
- The reaction velocity for layer 2 is zero.

Note also that unlike reaction rates for ammonia and nitrate-nitrogen, the reaction velocity for nitrite is assumed not to vary between fresh and salt water systems. Note also that this model assumes that the only reaction of NO_2 is nitrification to NO3. However, Wetzel (2001, pp. 217&513) indicates that denitrification occurs through NO_2. Any error
is assumed small due to the typically small concentration of NO_2.
Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 47

$$a_{11} = -K_{L12} - \frac{\kappa_{NO2}^2 \theta^{T\text{-}20}}{s} f_O - s - \varpi_2$$

Equation 48

$$a_{21} = K_{L12} + \varpi_2$$

Equation 49

$$a_{12} = K_{L12}$$

Equation 50

$$a_{22} = -K_{L12} - \varpi_2 - \frac{H_2}{\Delta t}$$

Equation 51

$$b_1 = -s\, C_{NO2,O}^{t+\Delta t} - \frac{\kappa_{NH4,1}^2 \theta^{T-20}}{s} f_O f_{NH4}\, f_{d1} C_{NH_4,1}^{t+\Delta t}$$

Equation 52

$$b_2 = -\frac{H_2 C_{NO2,2}^t}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 53

$$a_{22} = -K_{L12} - \varpi_2$$

Equation 54

$$b_2 = 0$$

The modification of the second-stage nitrification reaction by dissolved oxygen is computed from

Equation 55

$$f_O = \frac{O_{2,0}}{O_{2,0} + K_{NO2,O2}}$$

where

$O_{2,0}$ = dissolved oxygen concentration in the overlying water column, and
$K_{NO2,O2}$ = half-saturation concentration of dissolved oxygen in the second-stage nitrification reaction

Once the nitrite-concentrations have been updated, the flux to the water column is computed from:
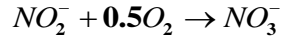
Equation 56

$$J_{NO2} = s\left(C_{NO2,1}^{t+\Delta t} - C_{NO2,0}\right)$$

where J_{NO2} is the nitrite flux to the water column. Note that in WASP, nitrite is not a state variable and the water column concentration is assumed to equal zero.
In order to compute the oxygen consumption due to the oxidation of ammonia in the aerobic layer, the second state of the nitrification reaction can be represented by (Chapra 1997)

Equation 57

$$NO_2^- + 0.5O_2 \rightarrow NO_3^-$$

so that the consumption of oxygen during the process can be represented by (Chapra 1997, Equation 23.4)

Equation 58

$$a_{no2} = \frac{0.5(32)}{14} = 1.14 \quad gO \quad gN^{-1}$$

Therefore the contribution of the oxidation of ammonia to SOD can be estimated from

Equation 59

$$NSOD_{NO2} = a_{no2} \frac{\kappa_{NO2,1}^2 \theta^{T-20}}{s} f_O C_{NO2,1}^{t+\Delta t}$$

Nitrate

The two-layer mass balance equations for nitrate are:

Layer 1

Equation 60

$$0 = -s\left(C_{NO3,1}^{t+\Delta t} - C_{NO3,O}^{t+\Delta t}\right) + K_{L12}\left(C_{NO3,2}^{t+\Delta t} - C_{NO3,1}^{t+\Delta t}\right) - \omega_2\ C_{NO3,1}^{t+\Delta t} - \frac{\kappa_{NO3,1}^2}{s}\ C_{NO3,1}^{t+\Delta t}$$

$$+ \frac{\kappa_{N02,1}^2 \theta^{T-20}}{s} f_O C_{NO2,1}^{t+\Delta t}$$

Layer 2

Equation 61

$$0 = -K_{L12}\left(C_{NO3,2}^{t+\Delta t} - C_{NO3,1}^{t+\Delta t}\right) + \omega_2(C_{NO3,1}^{t+\Delta t} - C_{NO3,2}^{t+\Delta t}) - \frac{H_2 C_{NO3,2}^{t+\Delta t}}{\Delta t}$$

$$-\kappa_{NO3,2} C_{NO3,2}^{t+\Delta t} + \frac{H_2 C_{NO3,2}^t}{\Delta t}$$

where all terms have been previously defined. Note that the primary difference between the general and nitrate equations is that there is no sorption so the total and dissolved concentrations are equal. For nitrate, there is a reaction velocity due to denitrification for both layers 1 and 2.

The second-stage nitrification rate becomes a source term for layer 1. Note also that there are two separate denitrification reaction velocities specified for each layer ($\kappa_{NO3,1}$ and $\kappa_{NO3,2}$), for fresh and salt waters with the one used based on the salinity (SAL) as compared to a salinity switch (SALTND, input).

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 62

$$a_{11} = -K_{L12} - \frac{\kappa_{NO3,1}^2 \theta^{T-20}}{s} - s - \omega_2$$

Equation 63

$$a_{21} = K_{L12} + \omega_2$$

Equation 64

$$a_{12} = K_{L12}$$

Equation 65

$$a_{22} = -K_{L12} - \kappa_{NO3,2}\theta^{T-20} - \omega_2 - \frac{H_2}{\Delta t}$$

Equation 66

$$b_1 = -s\ C_{NO3,O}^{t+\Delta t} - \frac{\kappa_{NO3,1}^2 \theta^{T-20}}{s} f_O C_{NO2,1}^{t+\Delta t}$$

Equation 67

$$b_2 = -\frac{H_2 C_{NO3,2}^t}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 68

$$a_{22} = -K_{L12} - \kappa_{NO3,2}\theta^{T-20} - \omega_2$$

Equation 69

$$b_2 = 0$$

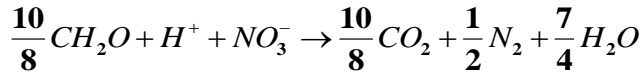Once the nitrate concentrations have been updated, the flux to the water column is computed from:

Equation 70

$$J_{NO3} = s\left(C_{NO3,1}^{t+\Delta t} - C_{NO3,0}\right)$$
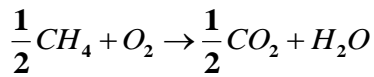
where J_{NO3} is the flux to the water column.
The process of denitrfication requires a carbon source as indicated by (Di Toro 2001, Equation 9.16)

Equation 71

$$\frac{10}{8}CH_2O + H^+ + NO_3^- \rightarrow \frac{10}{8}CO_2 + \frac{1}{2}N_2 + \frac{7}{4}H_2O$$

so that the carbon to nitrogen stoichiometric coefficient (a_{cn}) is 1.071 gC gN^{-1}. The oxidation of methane in the aerobic zone may be represented by

Equation 72

$$\frac{1}{2}CH_4 + O_2 \rightarrow \frac{1}{2}CO_2 + H_2O$$

so the oxygen to carbon stoichiometric coefficient (a_{oc}) is 2.67 g O g C^{-1}.
If all of the carbon produced by the diagenesis reaction was converted to methane and fully oxidized, the maximum SOD that could be produced would be

Equation 73

$$J_{O_2,C} = J_{C,2}^{t+\Delta t}$$

where in WASP, J_c is in oxygen equivalents.
However, this maximum is reduced by the carbon utilized during denitrification, so that the maximum oxygen utilization becomes

Equation 74

$$J_{O_2,C} = J_{C,2}^{t+\Delta t} - a_{oc} a_{cn} \left[\frac{\kappa_{NO3,1} \Theta^{T-20} C_{NO3,1}^{t+\Delta t}}{s} + \kappa_{NO3,2} \Theta^{T-20} C_{NO3,2}^{t+\Delta t} \right]$$

where $a_{oc}a_{cn}$ is 2.857.

Sulfides

Note that sulfide reactions are only computed in the WASP model for salt water systems (salinity greater than a salt switch, SALTSW). The two-layer mass balance equations for sulfide are:

Layer 1

Equation 75

$$0 = -s\left(f_{d1} C_{H2S,1}^{t+\Delta t} - C_{H2S,O}^{t+\Delta t} \right) + \omega_{12} \left(f_{p2} C_{H2S,2}^{t+\Delta t} - f_{p1} C_{H2S,1}^{t+\Delta t} \right) + K_{L12} \left(f_{d2} C_{H2S,2}^{t+\Delta t} - f_{d1} C_{H2S,1}^{t+\Delta t} \right)$$

$$-\omega_2 \ C_{H2S,1}^{t+\Delta t} - f_O \left[\frac{\kappa_{D,H2S,1}^2}{s} f_{d1} + \frac{\kappa_{P,H2S,1}^2}{s} f_{p1} \right] C_{H2S,1}^{t+\Delta t}$$

Layer 2

Equation 76

$$0 = -\omega_{12} \left(f_{p2} C_{H2S,2}^{t+\Delta t} - f_{p1} C_{H2S,1}^{t+\Delta t} \right) - K_{L12} \left(f_{d2} C_{H2S,2}^{t+\Delta t} - f_{d1} C_{H2S,1}^{t+\Delta t} \right) + \omega_2 (C_{H2S,1}^{t+\Delta t} - C_{H2S,2}^{t+\Delta t})$$

$$-\frac{H_2 C_{HS,2}^{t+\Delta t}}{\Delta t} + J_{HS,2}^{t+\Delta t} + \frac{H_2 C_{HS,2}^t}{\Delta t}$$

where all terms have been previously defined. Note that the primary difference between the ammonia and sulfide equations is that there are separate reaction velocities in layer 1 for the dissolved and particulate forms.

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 77

$$a_{11} = -\left(f_{d1} \right) K_{L12} - \left(f_{p1} \right) \omega_{12} - \frac{\left(\kappa_{HS,D}^2 f_{D,1} + \kappa_{HS,P}^2 f_{P,1} \right) \theta^{T-20}}{s} f_O - \left(f_{d1} \right) s - \omega_2$$

Equation 78

$$a_{21} = +\omega_{12} \left(f_{p1} \right) + K_{L12} \left(f_{d1} \right) + \omega_2$$

Equation 79

$$a_{12} = +\omega_{12}\left(f_{p2}\right) + K_{L12}\left(f_{d2}\right)$$

Equation 80

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2 - \frac{H_2}{\Delta t}$$

Equation 81

$$b_1 = 0$$

Equation 82

$$b_2 = -J_{OC} - \frac{H_2 C_{HS,2}^t}{\Delta t}$$

where the $J_{HS,2}$ flux (Equation 76) is expressed as an oxygen equivalent flux (J_{OC}) computed from Equation 74. For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 83

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2$$

Equation 84

$$b_2 = -J_{OC}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 85

$$f_{d1} = \frac{1}{1 + \pi_{HS,1} S_1}; f_{p1} = \frac{\pi_{HS,1} S_1}{1 + \pi_{HS,1} S_1}$$

$$f_{d2} = \frac{1}{1 + \pi_{HS,2} S_2}; f_{p1} = \frac{\pi_{HS,2} S_2}{1 + \pi_{HS,2} S_2}$$

where

$\pi_{HS,1}$ = partition coefficient for sulfides in layer 1
$\pi_{HS,2}$ = partition coefficient for sulfides in layer 2
$S1$ = solids concentration in layer 1
$S2$ = solids concentration in layer 2

The dissolved oxygen correction to the surface reaction is computed from (with KMHSO2 being the half-saturation constant for sulfide reaction),

Equation 86

$$f_O = \frac{O_{2,0}}{K_{MHS,O2}}$$

The primary other difference is that partition coefficients are specified separately for the two layers, so that

Equation 87

$$f_{d,1} = \frac{1}{1 + \pi_{H2S,1} S_1}; f_{p,1} = \frac{\pi_{H2S,1} S_1}{1 + \pi_{H2S,1} S_1}$$

Equation 88

$$f_{d,2} = \frac{1}{1 + \pi_{H2S,2} S_2}; f_{p,1} = \frac{\pi_{H2S,2} S_2}{1 + \pi_{H2S,2} S_2}$$

where
$\pi_{H2S,1}$ = partition coefficient for sulfide in layer 1
$\pi_{H2S,2}$ = partition coefficient for sulfide in layer 2
$S1$ = solids concentration in layer 1
$S2$ = solids concentration in layer 2

There is no external source term for sulfides in layer 1. The source term for layer 2 is computed from the carbon diagenesis term (Equation 74), in oxygen equivalents and corrected for denitrification, since denitrification requires a carbon source and is a sink for carbon. Once the sulfide concentrations have been updated, the flux to the water column is computed from:

Equation 89

$$J_{H2S} = s\, f_{D1} C_{H2S,1}^{t+\Delta t}$$

where J_{H2S} is the flux to the water column. The SOD due to carbonaceous demand is then computed from

Equation 90

$$CSOD_{HS} = \frac{\left(\kappa_{HS,D}^2 f_{D,1} + \kappa_{HS,P}^2 f_{P,1}\right)\theta^{T-20}}{s}\, f_O\, C_{H2S,1}^{t+\Delta t}$$

Methane

In WASP, methane fluxes are only computed for freshwater systems (where the salinity (SAL) is less than a specified quantity (SALTSW). The first consideration in the computation of methane fluxes is that the maximum methane production, in oxygen equivalents, is related to the carbon diagenesis (J_{OC}), corrected for denitrification (Equation 74). Assuming complete oxidation, the maximum carbonaceous SOD that can be exerted is (Chapra 2000, DiToro 2001)

Equation 91

$$CSOD_{max} = \sqrt{2K_{L12}C_S J_{O2}}$$

or (for computed $CSOD_{max} > J_{O2}$)

Equation 92

$$CSOD_{max} = J_{O2}$$

where K_{L12} was defined previously and C_s the saturation methane concentration, computed from (Di Toro 2001, Equation 10.51)

Equation 93

$$C_{CH4,SAT} = 100\left(1 + \frac{H_O}{10}\right)1.024^{(20-T)}$$

where H_o is the depth of the water column over the sediment. As indicated, if the computed $CSOD_{max}$ exceeds the available carbon flux (J_{OC} in oxygen equivalents and corrected for denitrification), then $CSOD_{max}$ is set equal to that flux ($CSOD_{max}=J_{OC}$).
The flux of dissolved methane at the sediment water interface can be computed from (Chapra 2000, Eq. 25.43; DiToro 2001 Eq. 10.32)

Equation 94

$$J_{out} = CSOD_{max}\ Sech(\lambda_c H_1)$$

where (Di Toro 2001, Equation 10.39)

Equation 95

$$\lambda_c H_1 = \frac{\kappa_{CH4,1}\theta^{(T-20)/2}}{s})$$

Note that the temperature correction in the above equation is reflected in the ICM code (Cerco and Cole 1995) and elsewhere. The the hyperbolic secant (Sech) is computed as

Equation 96

$$Sech(x) = \frac{2}{e^x + e^{-x}}$$

Methane may be oxidized, producing sediment oxygen demand, or exchanged with the water column in either gaseous or dissolved form. The carbonaceous SOD can be computed from

Equation 97

$$CSOD_{CH4} = CSOD_{max}(1 - Sech(\lambda_c H_1))$$

and the fluxes of dissolved and gaseous methane can be computed from

Equation 98

$$J[CH_4(aq)] = CSOD_{max} - CSOD_{CH4}; \quad J[CH_4(g)] = J_{OC} - J[CH_4(aq)] - CSOD_{CH4}$$

SOD

Once the concentrations of materials affecting oxygen are computed, and the stoichiometric relationships described above applied, the SOD is computed from

Equation 99

$$SOD = CSOD_{HS} + CSOD_{NH4} + CSOD_{NO2}$$

for salt water systems or

Equation 100

$$SOD = CSOD_{CH4} + CSOD_{NH4} + CSOD_{NO2}$$

for freshwater systems, where the oxygen demands due to sulfide (Equation 90), methane (Equation 97), and nitrification (Equation 44 and Equation 59) were defined previously. Note that in the iterative solution for s, the SOD computed this computational step is compared to that from the previous iteration, and as discussed above, if it differs by more than a specified amount, a new value of s is computed and the solution iterated.

Computation of phosphate and silica

As discussed above, the SOD is computed iteratively in order to determine the value of s (the surface sediment transfer rate). Once completed, the concentrations of phosphate and ammonia, which do not affect SOD, are computed. The computations for phosphate and silica are similar to those described above and briefly presented below.

Silica

The two-layer mass balance equations for silica are:

Layer 1
Equation 101

$$\mathbf{0} = -s\left(f_{d1}C_{Si,1}^{t+\Delta t} - C_{Si,O}^{t+\Delta t}\right) + \varpi_{12}\left(f_{p2}C_{Si,2}^{t+\Delta t} - f_{p1}C_{Si,1}^{t+\Delta t}\right)$$
$$+ K_{L12}\left(f_{d2}C_{Si,2}^{t+\Delta t} - f_{d1}C_{Si,1}^{t+\Delta t}\right) - \varpi_2\, C_{Si,1}^{t+\Delta t}$$
Layer 2

Equation 102

$$0 = -\omega_{12}\left(f_{p2}C_{Si,2}^{t+\Delta t} - f_{p1}C_{Si,1}^{t+\Delta t}\right) - K_{L12}\left(f_{d2}C_{Si,2}^{t+\Delta t} - f_{d1}C_{Si,1}^{t+\Delta t}\right) + \omega_2(C_{Si,1}^{t+\Delta t} - C_{Si4,2}^{t+\Delta t})$$

$$-\kappa_3 C_{Si,2}^{t+\Delta t} - \frac{H_2 C_{Si,2}^{t+\Delta t}}{\Delta t} + J_{Si,2}^{t+\Delta t} + \frac{H_2 C_{Si,2}^{t}}{\Delta t}$$

where all terms have been previously defined. Note that the primary difference between the general equations presented previously and the silica equations are there are no silica source terms or reactions in the aerobic layer. In the anaerobic layer (layer 2), the reaction rate is applied only to the dissolved fraction.

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 103

$$a_{11} = -\left(f_{d1}\right)K_{L12} - \left(f_{p1}\right)\omega_{12} - \omega_2$$

Equation 104

$$a_{21} = +\omega_{12}\left(f_{p1}\right) + K_{L12}\left(f_{d1}\right) + \omega_2$$

Equation 105

$$a_{12} = +\omega_{12}\left(f_{p2}\right) + K_{L12}\left(f_{d2}\right)$$

Equation 106

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2 - \kappa_3 - \frac{H_2}{\Delta t}$$

Equation 107

$$b_1 = -s\, C_{Si,O}^{t+\Delta t}$$

Equation 108

$$b_2 = -J_{Si}^{t+\Delta t} - \frac{H_2 C_{Si,2}^{t}}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 109

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2 - \kappa_3$$

Equation 110

$$b_2 = -J_{Si,2}^{t+\Delta t}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 111

$$f_{d1} = \frac{1}{1+\pi_{Si,1}S_1}; f_{p1} = \frac{\pi_{Si,1}S_1}{1+\pi_{Si,1}S_1}$$

$$f_{d2} = \frac{1}{1+\pi_{Si,2}S_2}; f_{p1} = \frac{\pi_{Si,2}S_2}{1+\pi_{Si,2}S_2}$$

where

$\pi_{Si,1}$ = partition coefficient for Silica in layer 1
$\pi_{Si,1}$ = partition coefficient for Silica in layer 2
S1 = solids concentration in layer 1
S2 = solids concentration in layer 2

The partition coefficient in the anaerobic layer is set to an input value. For layer 1, the aerobic layer, if the oxygen concentration in the overlying water column exceeds a critical concentration (specified in input) then the partition coefficient is increased to represent the trapping of silica, or sorption onto iron oxyhydroxide. If the dissolved oxygen is below the critical value, then the sorption coefficient in layer 1 goes to zero as in (Di Toro 2001, Eq. 7.18)

Equation 112

$$\pi_{Si,1} = \pi_{Si,2}\left(\Delta\pi_{Si,1}\right) \ for \left[O_2(0)\right] > \left[O_2(0)\right]_{crit,Si}$$

and

Equation 113

$$\pi_{Si,1} = \pi_{Si,2}\left(\Delta\pi_{Si,1}\right)^{\beta_{Si}} \ for \left[O_2(0)\right] \le \left[O_2(0)\right]_{crit,Si}$$

where $\beta_{PO4} = \dfrac{\left[O_2(0)\right]}{\left[O_2(0)\right]_{crit,PO4}}$

and $\Delta\pi_{Si}$ is a specified incremental change.

The expression for silica dissolution in the anaerobic layer, modified by the Michaelis-Menton dependency of the dissolution rate on particulate silica, is given by (Di Toro 2001, Eq. 7.16)

Equation 114

$$S_{Si} = k_{Si}\Theta^{(T-20)} \frac{P_{Si}}{P_{Si} + K_{m,PSi}} \left(C_{Si,sat} - f_{d,2}C_{Si,2}^{t+\Delta t} \right)$$

where
P_{Si} = the biogenic silica diagenesis flux to which detrital silica was added
$K_{m,PSi}$ = half saturation constant (KMPSI)
k_{Si} = rate of silica dissolution (KADSA from water quality model)
$C_{Si,sat}$ = saturation concentration for silica ($C_{SI,sat}$, an input value)
Based on Equation 114, the loss term (κ_3) and source term for the sediments ($J_{Si,2}^{t+\Delta t}$) are then specified as

Equation 115

$$\kappa_3 = k_{Si}\Theta^{(T-20)} f_{d,2} \frac{P_{Si}}{P_{Si} + K_{m,PSi}}$$

and

Equation 116

$$J_{Si,2}^{t+\Delta t} = k_{Si}\Theta^{(T-20)} \frac{P_{Si}}{P_{Si} + K_{m,PSi}} C_{Si,sat}$$

Once the silica concentrations have been updated, the flux to the water column is computed from:

Equation 117

$$J_{Si} = s\left(C_{Si,1}^{t+\Delta t} - C_{Si,0} \right)$$

where J_{Si} is the flux to the water column.

Phosphate

The two-layer mass balance equations for phosphate are:

Layer 1
Equation 118

$$0 = -s\left(f_{d1}C_{PO4,1}^{t+\Delta t} - C_{PO4,O}^{t+\Delta t} \right) + \omega_{12}\left(f_{p2}C_{PO4,2}^{t+\Delta t} - f_{p1}C_{PO4,1}^{t+\Delta t} \right)$$
$$+ K_{L12}\left(f_{d2}C_{PO4,2}^{t+\Delta t} - f_{d1}C_{PO4,1}^{t+\Delta t} \right) - \omega_2 C_{PO4,1}^{t+\Delta t}$$

Layer 2

Equation 119

$$0 = -\omega_{12}\left(f_{p2}C_{PO4,2}^{t+\Delta t} - f_{p1}C_{PO4,1}^{t+\Delta t}\right) - K_{L12}\left(f_{d2}C_{PO4,2}^{t+\Delta t} - f_{d1}C_{PO4,1}^{t+\Delta t}\right) + \omega_2(C_{PO4,1}^{t+\Delta t} - C_{PO44,2}^{t+\Delta t})$$
$$-\frac{H_2C_{PO4,2}^{t+\Delta t}}{\Delta t} + J_{PO4,2}^{t+\Delta t} + \frac{H_2C_{PO4,2}^t}{\Delta t}$$

where all terms have been previously defined. Note that the primary difference between the general equations presented previously and the phosphate equations are there are no reactions in either layer.

Based upon the two-layer mass balance equations above, the elements in the solution matrix then become:

Equation 120

$$a_{11} = -\left(f_{d1}\right)K_{L12} - \left(f_{p1}\right)\omega_{12} - (f_{d1})s - \omega_2$$

Equation 121

$$a_{21} = +\omega_{12}\left(f_{p1}\right) + K_{L12}\left(f_{d1}\right) + \omega_2$$

Equation 122

$$a_{12} = +\omega_{12}\left(f_{p2}\right) + K_{L12}\left(f_{d2}\right)$$

Equation 123

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2 - \frac{H_2}{\Delta t}$$

Equation 124

$$b_1 = -s\ C_{PO4,O}^{t+\Delta t}$$

Equation 125

$$b_2 = -J_{PO4,2}^{t+\Delta t} - \frac{H_2C_{PO4,2}^t}{\Delta t}$$

For the steady-state solution, an option in WASP used to compute the initial conditions, the elements of the matrix are modified as follows

Equation 126

$$a_{22} = -\omega_{12}\left(f_{p2}\right) - K_{L12}\left(f_{d2}\right) - \omega_2$$

Equation 127

$$b_2 = -J_{PO4,2}^{t+\Delta t}$$

The fraction dissolved and particulate in the two layers are computed from:

Equation 128

$$f_{d,1} = \frac{1}{1+\pi_{PO4,1}S_1}; \quad f_{p,1} = \frac{\pi_{PO4,1}S_1}{1+\pi_{PO4,1}S_1}$$

$$f_{d,2} = \frac{1}{1+\pi_{PO4,2}S_2}; \quad f_{p,1} = \frac{\pi_{PO4,2}S_2}{1+\pi_{PO4,2}S_2}$$

where

$\pi_{PO4,i}$	=	partition coefficient for silica in layer i (PIE2)
S1	=	solids concentration in layer 1 (M1)
S2	=	solids concentration in layer 2 (M2)

The partition coefficient in the anaerobic layer is set to an input value. For layer 1, the aerobic layer, if the oxygen concentration in the overlying water column exceeds a critical concentration (O2CRIT, specified in input) then the partition coefficient is increased to represent the trapping of phosphates, or sorption onto iron oxyhydroxide. If the dissolved oxygen is below the critical value, then the sorption coefficient in layer 1 goes to zero as in (Di Toro 2001, Eq. 6.19)

Equation 129

$$\pi_{PO4,1} = \pi_{PO4,2}\left(\Delta\pi_{PO4,1}\right) \ for \ \left[O_2(0)\right] > \left[O_2(0)\right]_{crit}$$

and

$$\pi_{PO4,1} = \pi_{PO4,2}\left(\Delta\pi_{PO4,1}\right)^{\beta_{PO4}} \ for \ \left[O_2(0)\right] \leq \left[O_2(0)\right]_{crit}$$

$$where \ \beta_{PO4} = \frac{\left[O_2(0)\right]}{\left[O_2(0)\right]_{crit,PO4}}$$

and $\Delta\pi_{PO4}$ is a specified incremental change (which is set to either a freshwateror saltwaterinput value).

The source term for layer 2 is a result of the phosphate produced by sediment diagenesis to which is added the flux of inorganic phosphorus from the water column. Once the phosphate concentrations have been updated, the flux to the water column is computed from:

Equation 130

$$J_{PO4} = s\left(C_{PO4,1}^{t+\Delta t} - C_{PO4,0}\right)$$

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Appendix B. Comparison of Ecology's SedFlux.xlsm with Professor James Martin's SED_JLM.FOR

The sediment flux model (SFM) developed for the USEPA WASP model has previously undergone rigorous review and testing (Martin 2002). Professor James Martin at Mississippi State University Ecology has developed a standalone testing tool called SED_JLM.FOR that provides identical results compared with the WASP SFM. Ecology, in collaboration with Dr. Martin, has also developed an Excel VBA version of the SFM model called 'SedFlux.xlsm' that predicts nearly identical results (same within +/- 0.001%) compared with the SED_JLM.FOR for both time-variable and steady-state solutions (Ecology, 2013).

This appendix documents the results of comparison of Martin's SED_JLM.FOR with Ecology's SedFlux.xlsm tool for the time-variable model using the following test inputs using a model time step of 0.01 days:

Deposition fluxes from overlying water into the sediment:
Jcin = 0.3 gO2/m^2/d (deposition of POC)
Jnin = 0.005 gN/m^2/d (deposition of PON)
Jpin = 0.003 gP/m^2/d (deposition of POP)

Overlying water quality:
O20 = 5 mg/L (dissolved oxygen)
Depth = 2 m (depth of water)
Tw = 15 deg C (temperature)
NH30 = 0.015 mgN/L (ammonium N)
NO30 = 0.1 mgN/L (nitrate + nitrite)
PO40 = 0.004 mgP/L (soluble reactive P)
CH40 = 0 mg/L (dissolved organic C)
SALw = 30 psu (salinity)

Table 1 presents the assumed initial conditions. Table 2 presents the assumed kinetic rate parameter values. Figures B-1 through B-10 show the comparison of results for SED_JLM and SedFlux.xlsm.

Table B-1. SedFlux.xls - Input of initial conditions (only used for Time Variable 2 option)

Name	Symbol	Units	Input value
Particulate organic C, N, and P in layer 2			
G class 1 POC in layer 2	POC2(1)	gO2/m^3	100.000
G class 2 POC in layer 2	POC2(2)	gO2/m^3	800.000
G class 3 POC in layer 2	POC2(3)	gO2/m^3	9100.000
G class 1 PON in layer 2	PON2(1)	gN/m^3	10.000
G class 2 PON in layer 2	PON2(2)	gN/m^3	80.000
G class 3 PON in layer 2	PON2(3)	gN/m^3	910.000
G class 1 POP in layer 2	POP2(1)	gP/m^3	2.500
G class 2 POP in layer 2	POP2(2)	gP/m^3	20.000
G class 3 POP in layer 2	POP2(3)	gP/m^3	227.500
Dissolved constituents in layer 1 and 2 porewater			
Dissolved ammonia N in layer 1 porewater	NH3(1)	mgN/L	0.000
Dissolved ammonia N in layer 2 porewater	NH3(2)	mgN/L	0.000
Dissolved nitrate+nitrite N in layer 1 porewater	NO3(1)	mgN/L	0.000
Dissolved nitrate+nitrite N in layer 2 porewater	NO3(2)	mgN/L	0.000
Dissolved phosphate P in layer 1 porewater	PO4(1)	mgP/L	0.000
Dissolved phosphate P in layer 2 porewater	PO4(2)	mgP/L	0.000

Table B-2. SedFlux.xls - Input of rate parameter values

| Name	Symbol	Units	Input value
solids concentration in aerobic layer 1	m1	kgD/L	0.5
solids concentration in anaerobic layer 2	m2	kgD/L	0.5
bioturbation particle mixing coefficient	Dp	m^2/d	0.00006
pore water diffusion coefficient	Dd	m^2/d	0.0025
deep burial velocity	w2	m/d	6.85E-06
thickness of sediment anaerobic layer 2	H2	m	0.1
Reaction velocities			
freshwater nitrification velocity	KappaNH3f	m/d	0.1313
saltwater nitrification velocity	KappaNH3s	m/d	0.1313
freshwater denitrification velocity in layer 1	KappaNO3_1f	m/d	0.1
saltwater denitrification velocity in layer 1	KappaNO3_1s	m/d	0.1
denitrfication in the anaerobic layer 2	KappaNO3_2	m/d	0.025
methane oxidation in the aerobic layer 1	KappaCH4	m/d	0.7
Half saturation constants			
nitrification half saturation for NH4N	KM_NH3	mgN/L	0.728
nitrification half saturation for O2	KM_O2_NH3	mgO2/L	0.37
Partitioning coefficients			
partition coefficient for NH4 in layer 1 and 2	KdNH3	L/kgD	1
partition coefficient for PO4 in layer 2	KdPO42	L/kgD	20
freshwater factor that increases the aerobic layer partition coefficient of inorganic P	dKDPO41f	unitless	20
saltwater factor that increases the aerobic layer partition coefficient of inorganic P	dKDPO41s	unitless	20
critical O2 concentration in layer 2 for adjustment of partition coefficient for inorganic P	O2critPO4	mgO2/L	2
Temperature coefficients			
temperature theta for bioturbation mixing between layers 1 and 2	ThtaDp	unitless	1.117
temperature theta for pore water diffusion between layers 1 and 2	ThtaDd	unitless	1.08
temperature theta for nitrification	ThtaNH3	unitless	1.123
temperature theta for denitrification	ThtaNO3	unitless	1.08
temperature theta for methane oxidation	ThtaCH4	unitless	1.079
Salinity thresholds			
salinity above which sulfide rather than methane is produced from C diagenesis	SALTSW	psu	1
salinity above which saltwater nitrification/denitrification rates are used for aerobic layer	SALTND	psu	1
Sulfide constants			
aerobic layer reaction velocity for dissolved sulfide oxidation	KappaH2Sd1	m/d	0.2
aerobic layer reaction velocity for particulate sulfide oxidation	KappaH2Sp1	m/d	0.4
temperature coefficient for sulfide oxidation	ThtaH2S	unitless	1.079
sulfide oxidation normalization constant for O2	KMHSO2	mgO2/L	4
partition coefficient for sulfide in aerobic layer 1	KdH2S1	L/kgD	100
partition coefficient for sulfide in anaerobic layer 2	KdH2S2	L/kgD	100
Fractions of G classes 1 and 2 for settling PON, POC, and POP			
fraction of class 1 pon	frpon1	unitless	0.65
fraction of class 2 pon	frpon2	unitless	0.25
fraction of class 1 poc	frpoc1	unitless	0.65
fraction of class 2 poc	frpoc2	unitless	0.2
fraction of class 1 pop	frpop1	unitless	0.65
fraction of class 2 pop	frpop2	unitless	0.2
Diagenesis rate constants for G clase 1, 2, and 3 N/C/P			
G class 1 pon mineralization	kpon1	day^-1	0.035
G class 2 pon mineralization	kpon2	day^-1	0.0018
G class 3 pon mineralization	kpon3	day^-1	0
G class 1 poc mineralization	kpoc1	day^-1	0.035
G class 2 poc mineralization	kpoc2	day^-1	0.0018
G class 3 poc mineralization	kpoc3	day^-1	0
G class 1 pop mineralization	kpop1	day^-1	0.035
G class 2 pop mineralization	kpop2	day^-1	0.0018
G class 3 pop mineralization	kpop3	day^-1	0
Temperature coefficients for G class 1, 2, and 3 mineralization			
temperature theta for G class 1 pon	ThtaPON1	unitless	1.1
temperature theta for G class 2 pon	ThtaPON2	unitless	1.15
temperature theta for G class 3 pon	ThtaPON3	unitless	1.17
temperature theta for G class 1 poc	ThtaPOC1	unitless	1.1
temperature theta for G class 2 poc	ThtaPOC2	unitless	1.15
temperature theta for G class 3 poc	ThtaPOC3	unitless	1.17
temperature theta for G class 1 pop	ThtaPOP1	unitless	1.1
temperature theta for G class 2 pop	ThtaPOP2	unitless	1.15
temperature theta for G class 3 pop	ThtaPOP3	unitless	1.17
Parameters for partical mixing and benthic stress			
reference G1 at which w12base = Dp / H2 at 20 degC for DiToro eqn 13.1	POC1R	gO2/m^3	0.2667
first-order decay rate constant for benthic stress (d^-1) for DiToro eqn 13.3	kBEN_STR	day^-1	0.03
particle mixing half-saturation constant for O2 (mgO2/L)	KM_O2_Dp	mgO2/L	4
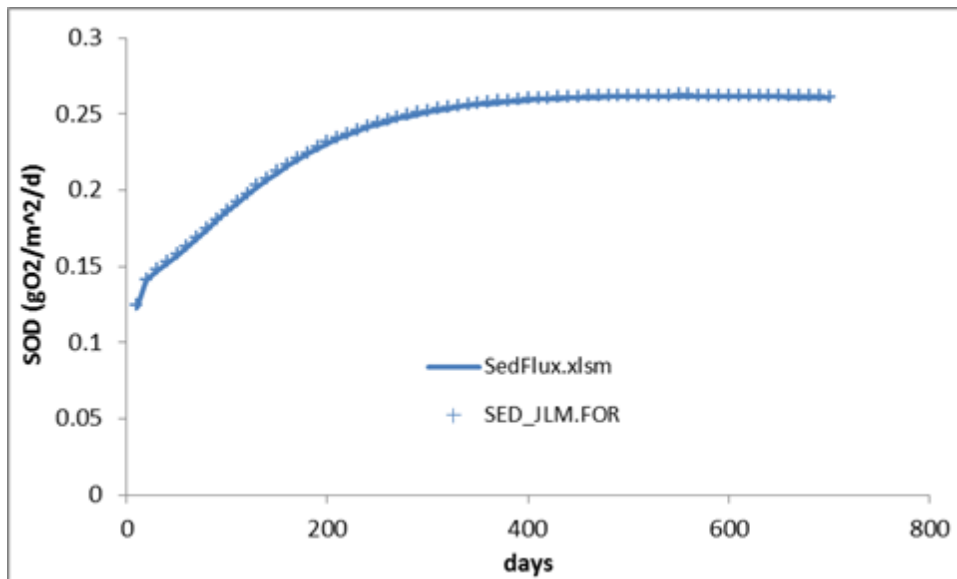
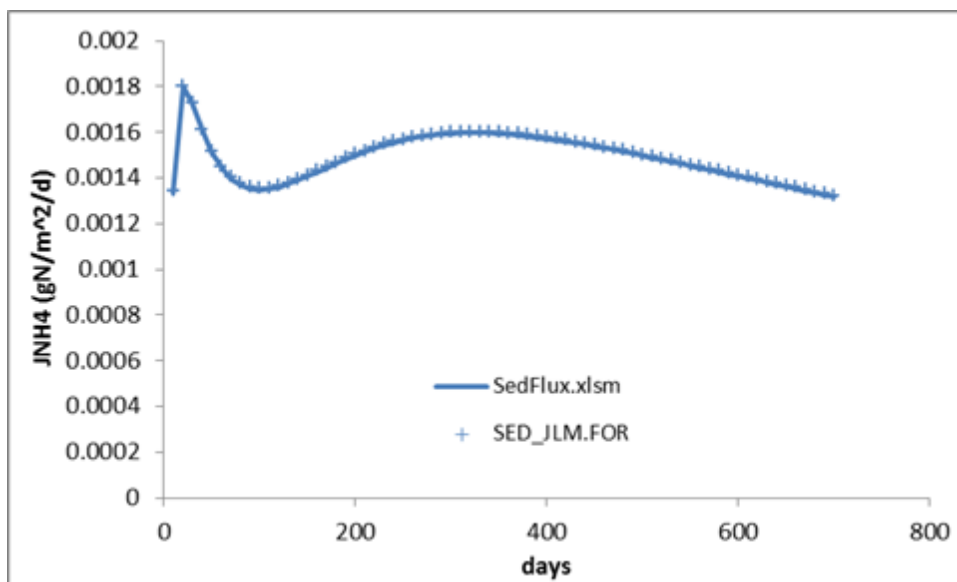Figure B-1. Sediment oxygen demand (SOD) (positive is flux from water into sediment)

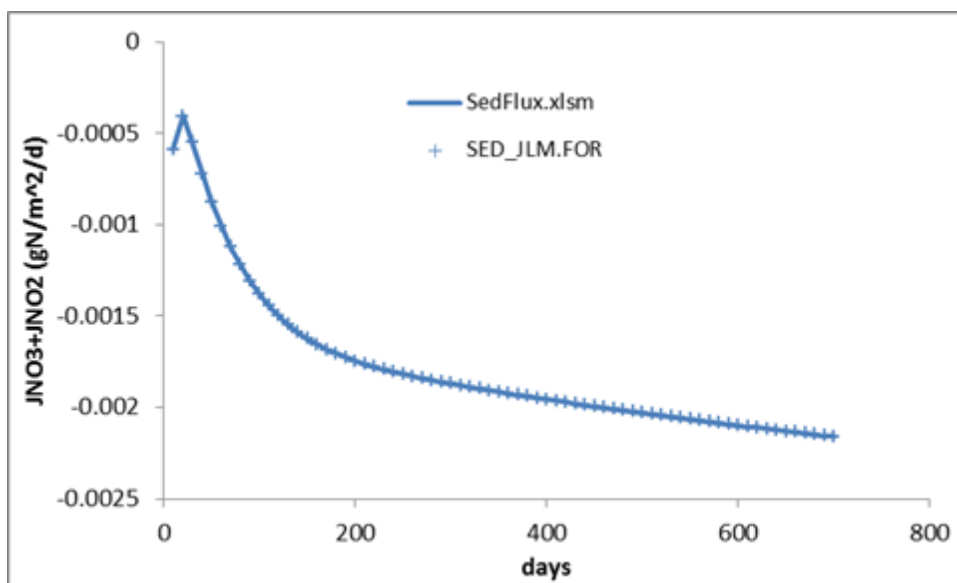Figure B-2. Sediment-water flux of ammonium (JNH4) (positive is flux from sediment into water).

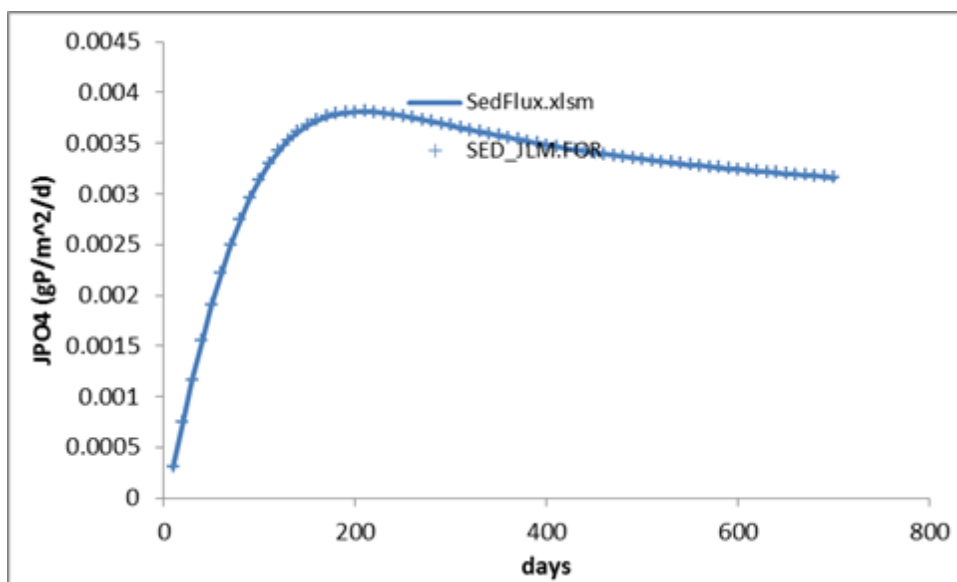Figure B-3. Sediment-water flux of nitrate+nitrite (JNO3+JNO2) (negative is flux from water into sediment).

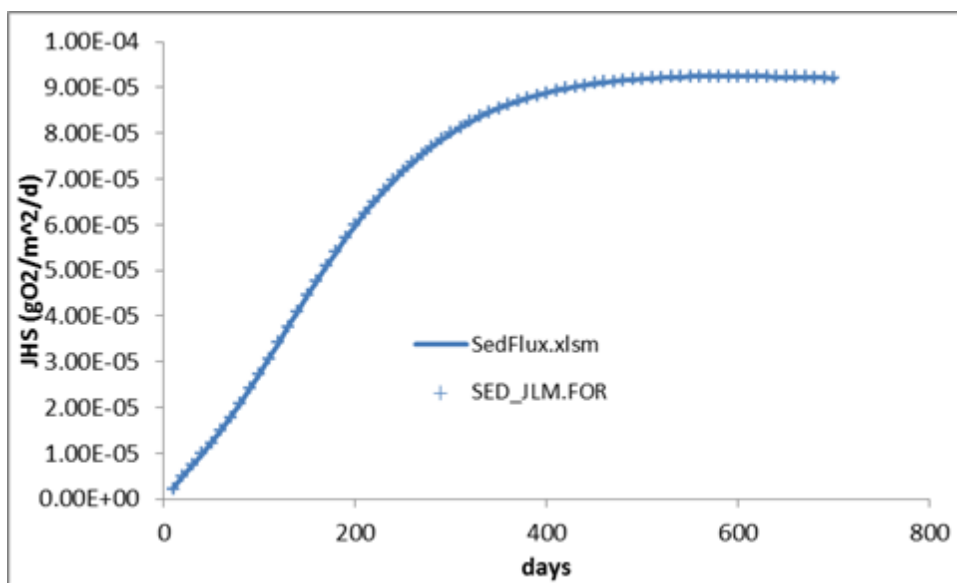Figure B-4. Sediment-water flux of phosphate (JPO4) (positive is flux from sediment into water).

Figure B-5. Sediment-water flux of sulfide (JHS) (positive is flux from sediment into water).
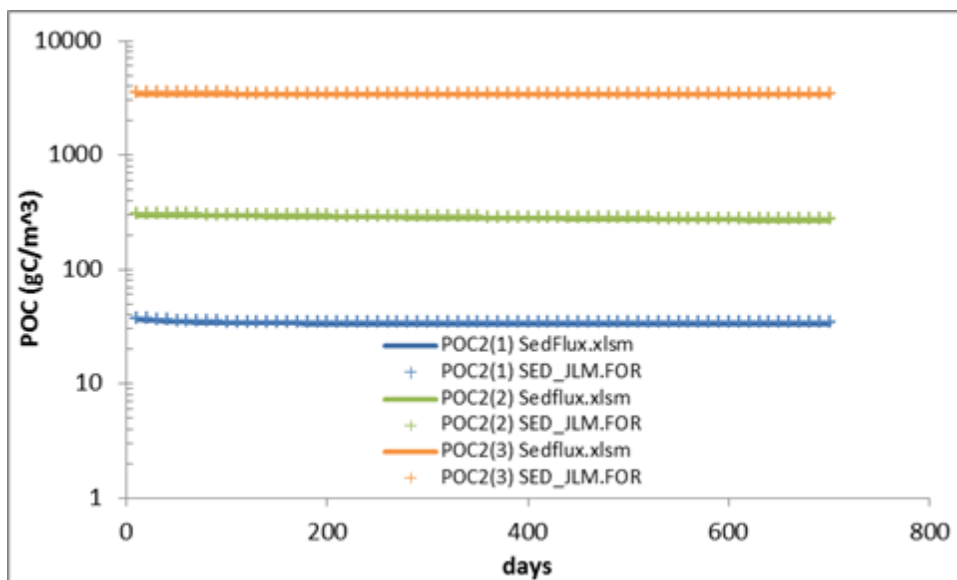
Figure B-6. Sediment layer 2 G-classes of particulate organic C (POC). POC in layer 2 in G class 1 is POC2(1), G class 2 is POC2(2), and G class 3 is POC2(3).
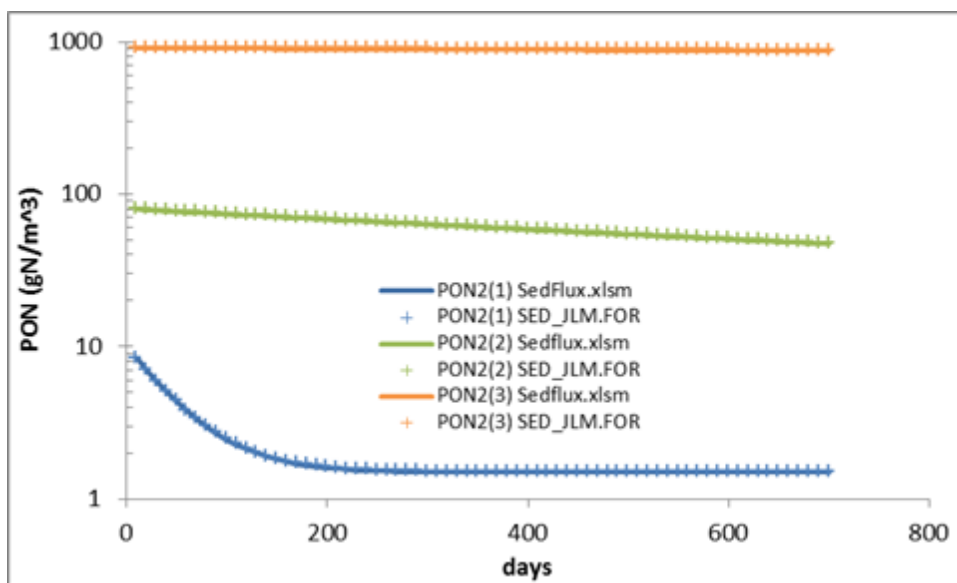
Figure B-7. Sediment layer 2 G-classes of particulate organic N (PON). PON in layer 2 in G class 1 is PON2(1), G class 2 is PON2(2), and G class 3 is PON2(3).
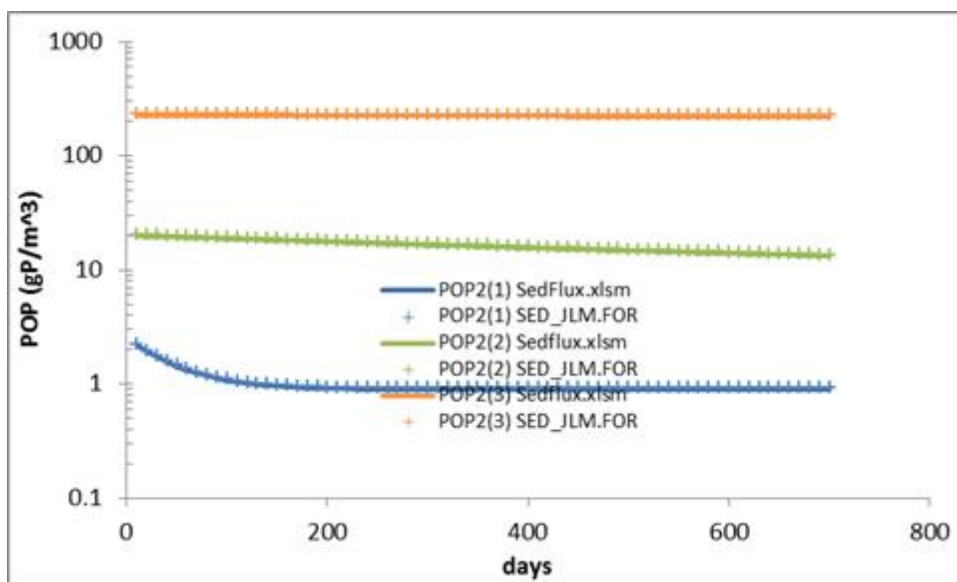

Figure B-8. Sediment layer 2 G-classes of particulate organic P (POP). POP in layer 2 in G class 1 is POP2(1), G class 2 is POP2(2), and G class 3 is POP2(3).
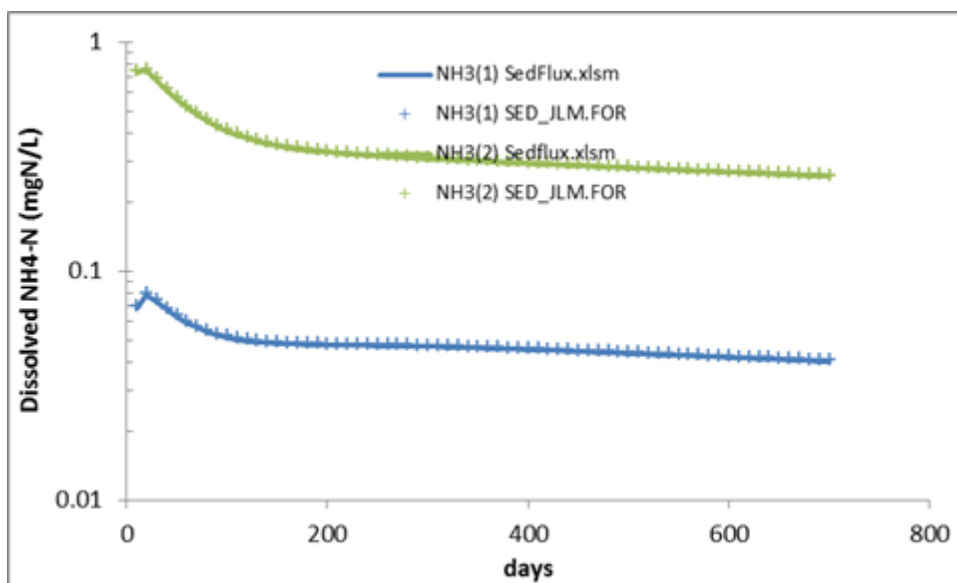
Figure B-9. Dissolved ammonium in sediment pore water in layer 1 (NH3(1)) and layer 2 (NH3(2)).
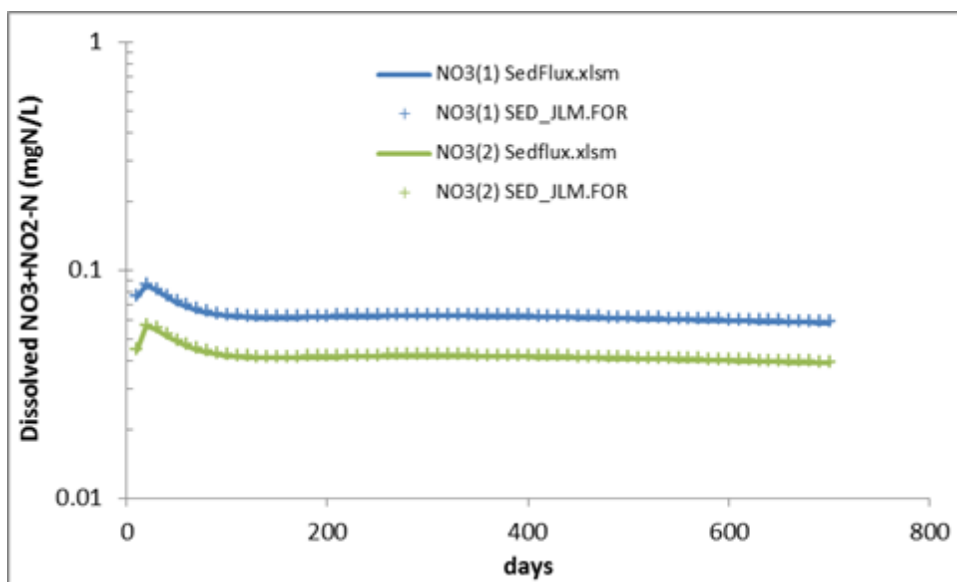

Figure B-10. Dissolved nitrate+nitrite in sediment pore water in layer 1 (NO3(1)) and layer 2 (NO3(2)).
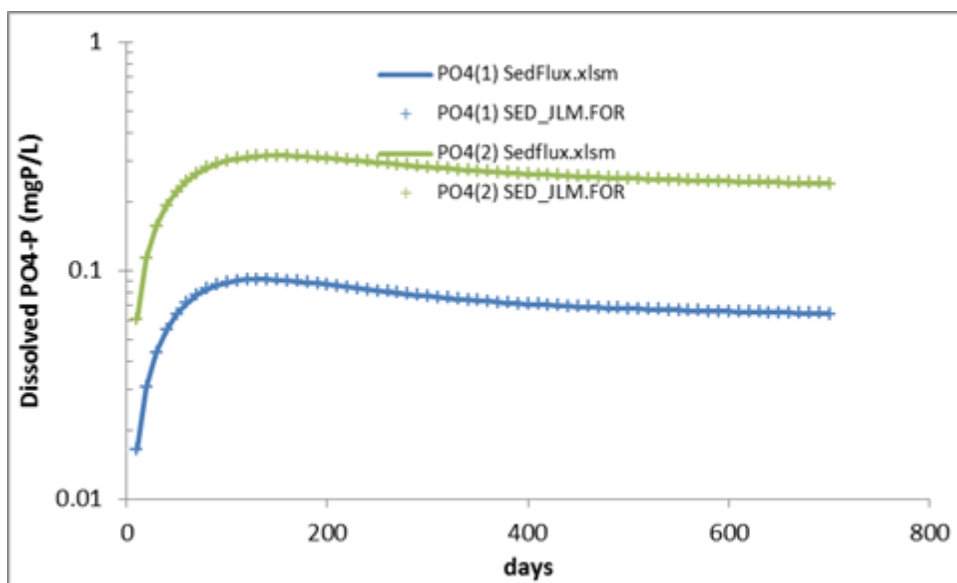
Figure B-11. Dissolved phosphate in sediment pore water in layer 1 (PO4(1)) and layer 2 (PO4(2)).

Appendix C. Glossary, Acronyms, and Abbreviations

Glossary

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Effluent: An outflowing of water from a natural body of water or from a man-made structure. For example, the treated outflow from a wastewater treatment plant.

Eutrophic: Nutrient- rich and high in productivity resulting from human activities such as fertilizer runoff and leaky septic systems.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities. This includes, but is not limited to, atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

Nutrient: Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will,

or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Streamflow: Discharge of water in a surface stream (river or creek).

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standard and are not expected to improve within the next two years.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

C	Carbon
DIN	Dissolved inorganic nitrogen (sum of nitrate, nitrite, and ammonium)
DOC	Dissolved organic carbon
e.g.	For example
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
et al.	And others
FVCOM	Finite-volume Coastal Ocean Model
ICM	Integrated Compartment Model
i.e.	In other words
MQO	Measurement quality objective
N	Nitrogen
NPDES	(See Glossary above)
PNNL	Pacific Northwest National Laboratory
POM	Princeton Ocean Model
QA	Quality assurance

RMSE	Root mean square error
SOD	Sediment oxygen demand
TMDL	(See Glossary above)
TOC	Total organic carbon
WAC	Washington Administrative Code
WRIA	Water Resource Inventory Area
WWTP	Wastewater treatment plant

Units of Measurement

m^3/s	cubic meters per second, a unit of flow
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
kg/d	kilograms per day
m	meter
mgd	million gallons per day
mg/L	milligrams per liter (parts per million)
mL	milliliters
mmol	millimole or one-thousandth of a mole
mole	an International System of Units (IS) unit of matter
psu	practical salinity units
ug/L	micrograms per liter (parts per billion)